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## **Graphical Abstract**

Highly thermal stable quinazoline-centered derivatives with tunable electron-only or bipolar nature were employed as host materials to achieve high efficient red phosphorescent organic light-emitting diodes.



# Synthesis, Photophysical and Optoelectronic Properties of Quinazoline-Centered Dyes and their Applications in Organic Light-Emitting Diodes

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**ABSTRACT:** Quinazoline-centered derivatives with benzoimidazole, carbazole, and triphenylene moieties, were synthesized. Their relationships between electrochemical, photophysical, and optoelectronic properties and structure were discussed in detail. Efficient red phosphorescent organic light-emitting diodes with low turn-on voltage were demonstrated by using them as host materials, and achieved maximum external quantum efficiencies, current efficiencies, and power efficiencies of 19.2%, 18.3 cd/A, 21.7 lm/W for 4-[4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl]-2-[3-(tri-phenylen-2-yl)phen-3-yl]quinazoline, of 18.4%, 17.6 cd/A, 19.3lm/W for 4-(9-phenyl-9H-carbazol-3-yl)-2-[3-(triphenylen-2-yl)phenyl]quinazoline, and of 15.6%, 14.4 cd/A, 16.7 lm/W for 2,4-bis[4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl]-1*H*-benzo[*d*]imidazol-2-yl)phenyl]-1*H*-benzo[*d*]imidazol-2-yl)phenyl]-2-[3-(triphenylen-2-yl)phenyl]quinazoline, of 15.6%, 14.4 cd/A, 16.7 lm/W for 2,4-bis[4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl]-1*H*-benzo[*d*]imidazol-2-yl)phenyl]-1*H*-benzo[*d*]imidazol-2-yl)phenyl]quinazoline, of 15.6%, 14.4 cd/A, 16.7 lm/W for 2,4-bis[4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl]quinazoline, and of 17.4%, 16.7 cd/A, 15.7 lm/W for 2,4-bis(9-phenyl-9H-carbazol-3-yl)quinazoline, respectively.

Moreover, improving the electron-injection/transport abilities of host materials could ideally improve the performance of organic light-emitting diodes under low operation voltage, while enhancement of hole-transporting abilities by using bipolar materials could balance the carriers to maintain high efficiency under high operating voltage. These materials exhibited high glass-transition temperature of 146-154  $^{\circ}$ C and decomposition temperature of 400-447  $^{\circ}$ C.

Keywords: Synthesis, Photophysical Property, Organic light-emitting diodes, Quinazoline Dyes

#### 1. INTRODUCTION

During the past two decades, organic light-emitting diodes (OLEDs) have been aroused intensive interests due to their potential applications in solid-state lighting and flexible panel displays.<sup>1-7</sup> Compared to the conventional fluorescent OLEDs, great research efforts have been devoted to development of phosphorescent OLEDs (PhOLEDs) because they can mostly approach 100% internal quantum efficiency by harvesting both singlet and triplet excitons when they incorporate appropriate transition metal-centered phosphorescent dopants as triplet emitters.<sup>8+11</sup> Typically, in order to reduce the severe concentration quenching and triplet-triplet annihilation (TTA), the emitters are usually doped with suitable host materials.<sup>12-13</sup> Carbazole-based derivatives were the most popular host materials for PhOLEDs due to their intrinsic high triplet energy, attractive hole mobilities and good hole-transporting properties.<sup>14</sup> On the other hand, molecules with electron-transporting feature based on oxadiazole, triazine, phenanthroline, and benzoimidazole units are used widely as functional groups that facilitate electron injection and transport.<sup>15</sup> Up to now, numerous efforts have been carried out to develop efficient host materials for red PhOLEDs to improve the efficiencies of EL devices.<sup>16-26</sup> A balanced charge carrier recombination is required to achieve high efficiency, while the electron mobilities are usually much lower than the hole mobilities in

OLEDs.<sup>27-28</sup> Thus, a host with bipolar features is highly desired to achieve both high and balanced charge transporting ability. Benzoimidazole/carbazole hybrid bipolar material, CPhBzIm<sup>29</sup> exhibited an excellent bipolar charge transport ability, and was employed to achieve highly efficient electrophosphorescence and two-color-based white OLEDs. Recently Wang's and Chen's groups co-reported a new simple carbazole-N-benzoimidazole-based bipolar material, mNBICz<sup>30</sup>, which was utilized as a host for PhOLED to demonstrate very high efficiencies too. However, mNBICz exhibits a low glass transition temperature  $(T_s)$  only at 86 °C mainly due to its low molecular weight. Adachi's group developed an efficient triphenylene-based electron transport materials Bpy-TP2, which have both high electron mobility and durability. Additional, Bpy-TP2-based OLED showed a significantly lower driving voltage, achieving lower power consumption when compared with conventional electron transport materials (ETMs) such as aluminium tris(quinolin-8-olate) (Alq<sub>3</sub>) and 1,3,5-tris(2-phenyl-1H-benzo[d]imidazol-1-yl)benzene (TPBi).<sup>31</sup> Pyridine is expected to be an electron deficient unit which has been used to construct novel cyclometalated organic ligands and electron-transporting materials, as well as pyrimidine and quinazoline derivatives.<sup>32</sup> Su's group developed a series of pyridine-containing ETMs,<sup>33</sup> and their energy levels of relative materials could be tuned by introduction of pyridine rings with various of nitrogen atom orientation. These materials had become the most popular ETMs to achieve highly efficient PhOLEDs. Quinazoline-based derivatives have attracted our interest due to their application on a novel approach of white OLED controlled by protonation<sup>34</sup> and their promising photophysical properties with potential application on colorimetric pH sensors.<sup>35</sup> On the other hand, as a branch of pyridine-containing materials, they are expected to exhibit potential applications on organic electronics.

In this paper we described synthesis of four new quinazoline-centered derivatives, 4-[4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl]-2-[3-(tri-phenylen-2-yl)phen-3-yl]quinazoline

(BITpQz),	4-(9-phenyl-9H-carbazol-3-yl)-2-[3-(triphenylen-2-yl)ph	enyl]quinazoline	(CzTpQz),
2,4-bis[4-(1-p	henyl-1 <i>H</i> -benzo[ <i>d</i> ]imidazol-2-yl)phenyl]quinazoline	(BBIQz),	and
2,4-bis(9-pher	nyl-9H-carbazol-3-yl)quinazoline (BCzQz) with benzoimid	azole, carbazole, an	d triphenylene
moieties, resp	ectively. Electrochemical, quantum calculation, photophysi	ical, and optoelectro	onic properties
were discusse	ed in detail as well as structure-properties relationship.	The HOMO prefer	to locate on
electron-donat	ting segment, while the LUMO is mostly dispersed	on quinazoline	or on strong
electron-accep	oting unit. Different substituents resulted in their tunab	le and promising	optoelectronic
properties. Co	omparatively, some important merits of multi-layer device	s such as carrier ba	lance, exciton
confinement,	and energy-barrier reduction ensured the performance of	f devices. On the	basis of these
materials as he	ost, efficient red PhOLEDs with low turn on voltage were do	emonstrated.	

#### 2. EXPERIMENTAL SECTION

General methods. chemicals 2,4-dichloroquinazoline, The reagents and such as (4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)boronic acid (1), 9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (2), and 4,4,5,5-tetramethyl-2-(3-(triphenylen-2-yl)phenyl)-1,3,2-dioxaborolane (5) were used as received unless otherwise. noted The auxiliary materials for OLED fabrication such as N,N'-diphenyl-N,N'-bis(9-phenyl-9H-carbazol-3-yl)-[1,1'-biphenyl]-4,4'-diamine (H04), 4,4',4"-tris(N-carbazolyl)triphenylamine (TCTA), TPBi were purchased from Yurui (Shanghai) Chemical Iridium(III)bis(4-methyl-2-(3,5-dimethylphenyl)quinolinato-N,C2') Co. Ltd. acetylacetonate and (Ir(mphmq)<sub>2</sub>acac) was purchased from Ningbo Intimechem Co. Ltd., and were purified further by vacuum sublimation prior to use. Nuclear magnetic resonance (NMR) spectral data of <sup>1</sup>H NMR and <sup>13</sup>C NMR were

recorded on Bruker AV-500 spectrometer with CDCl<sub>3</sub> or dimethyl suloxide- $d_6$  as deuterium solvent. Mass spectra (MS) were obtained on a Finnigan/Thermo Quest MAT 95XL instrument. Elemental analyses (CHN) were performed with Elemental Vario EL III instrument. UV-Vis absorption spectra were recorded on UV-2501PC instrument, while photoluminescence (PL) spectra were taken using FLSP920 fluorescence spectrophotometer, both in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution and in solid state, respectively, and PL quantum efficiency was measured by using a six inch integrating sphere. The glass transition temperatures (T<sub>g</sub>) of compounds were determined under a nitrogen atmosphere by differential scanning calorimetry (DSC) on Netzstch STA409PC using a scanning rate of 10 °C /min with nitrogen flushing. The decomposition temperature (T<sub>d</sub>) corresponding to 5% weight loss was conducted on a Perkin-Elmer Pyris 1 TGA thermal analyzer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out using a CH Instrument 660C electrochemical analyzer and with Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode as state reference electrode, with tetra(*n*-butyl)ammonium *hexa*-fluorophosphate (TBAPF<sub>6</sub>) in DMF as supporting electrolytes.

General procedure of Suzuki coupling reaction. 2,4-Dichloroquinazoline (5 g, 25 mmol), arylboronic acid, palladium acetate (113 mg, 0.5 mmol), triphenylphosphine (264 mg, 1 mmol) and potassium carbonate (10.4 g, 75.4 mmol) were suspended in a mixture of 1,4-dioxane (60 mL) and water (30 mL) in a three-necked, round-bottomed flask with tightly sealed. The mixture was stirred and heated at 100 °C for 12 hours under nitrogen atmosphere. After cooling to room temperature,  $CH_2Cl_2$  (50 mL) and water (50 mL) were added. The aqueous layer was extracted with  $CH_2Cl_2$  (3 × 20 mL). The combined organic layers were washed by brine (3 × 30 mL), dried over anhydrous sodium sulfate and solvents were removed under reduced pressure to yield the crude product as a light yellow solid, which was further purified by

recrystallization (dichloromethane/ethanol) to give pure product.

*2,4-Bis*[*4-(1-phenyl-1H-benzo*[*d*]*imidazol-2-yl*)*phenyl*]*quinazoline (BBIQz*) was synthesized according to the general procedure from 2,4-dichloroquinazoline (5 g, 25 mmol) and **1** (55.4 mmol) in 71% isolated yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *δ*): 8.62 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.93 (t, *J* = 7.0 Hz, 2H), 7.89 (t, *J* = 7.5 Hz, 1H), 7.85-7.81 (m, 4H), 7.74 (d, *J* = 9.5 Hz, 2H), 7.58-7.47 (m, 7H), 7.42-7.34 (m, 6H), 7.33-7.27 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, *δ*): 159.4, 152.1, 152.0, 151.5, 143.1, 143.1, 138.9, 138.3, 137.5, 137.4, 137.0, 136.9, 133.9, 131.8, 131.6, 130.2, 130.1, 130.0, 129.7, 129.5, 129.3, 128.9, 128.6, 128.5, 127.5, 127.5, 126.8, 123.7, 123.5, 123.3, 123.1, 121.6, 120.0, 120.0, 110.6, 110.5; MS (*m*/*z*, EI) Calcd for C<sub>46</sub>H<sub>30</sub>N<sub>6</sub> 666.25, found: 666.20. Anal. calcd. for C<sub>46</sub>H<sub>30</sub>N<sub>6</sub>: C 82.86, H 4.54, N, 12.60; Found: C 82.74, H 4.53, N, 12.61.

[4-(1-Phenyl-1H-benzo[d]imidazol-2-yl)phenyl]-2-chloroquinazoline (3) was synthesized according to the general procedure from 2,4-dichloroquinazoline (5 g, 25 mmol) and 1 (25 mmol) in 79% isolated yield as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.08 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.95-7.91 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.57-7.50 (m, 3H), 7.39-7.36 (m, 3H), 7.32-7.27 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ): 172.1, 157.1, 153.2, 142.3, 141.6, 137.1, 134.6, 130.1, 128.4, 128.0, 127.8, 127.6, 127.2, 126.8, 123.7, 123.2, 123.1, 121.9, 120.7, 110.2, 110.0.

4-[4-(1-Phenyl-1H-benzo[d]imidazol-2-yl)phenyl]-2-[3-(tri-phenylen-2-yl)phen-3-yl]quinazoline (BITpQz) was synthesized according to the general procedure from **3** (5 g, 11.5mmol) and **5** (4.97g, 11.5 mmol) in 88% isolated yield as white solid (7.2 g). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.10 (s, 1H), 8.94 (s, 1H), 8.78 (t, J = 3.5 Hz, 1H), 8.72 (t, J = 7.5 Hz, 2H), 8.65 (m, 3H), 8.20 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 7.5 Hz, 1H), 8.00 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.90 (m, 4H), 7.85 (d, J = 8.5 Hz, 2H), 7.66 (m, 5H), 7.55 (t, J = 7.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.41 (m, 3H), 7.32 (t, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ ): 137.5, 136.9, 133.8, 131.5, 130.3, 130.1, 130.1, 130.0, 129.9, 129.8, 129.7, 129.5, 129.3, 129.2, 129.0, 128.9, 127.9, 127.6, 127.5, 127.3, 127.3, 127.3, 127.3, 127.2, 126.8, 126.6, 123.9, 123.8, 123.5, 123.4, 123.4, 123.3, 123.3, 122.0, 121.7, 120.0, 110.6; MS (m/z, EI) Calcd for C<sub>51</sub>H<sub>32</sub>N<sub>4</sub> 700.26, found: 700.20. Anal. calcd. for C<sub>51</sub>H<sub>32</sub>N<sub>4</sub>: C 87.40, H 4.60, N, 7.99; Found: C 86.30, H 4.90, N, 7.63.

2,4-Bis(9-phenyl-9H-carbazol-3-yl)quinazoline (BCzQz) was synthesized according to the general procedure from 2,4-dichloroquinazoline (5 g, 25 mmol) and 2 (55.4 mmol) in 67% isolated yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 9.59 (s, 1H), 8.90 (d, *J* = 8.5 Hz, 1H), 8.77 (s, 1H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.29 (t, *J* = 8.5 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.90 (t, *J* = 7.0 Hz, 1H), 7.69-7.62 (m, 9H), 7.56-7.49 (m, 6H), 7.44 (m, 2H), 7.39-7.33 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ): 152.4, 142.6, 141.9, 141.6, 141.6, 137.6, 137.4, 133.3, 130.6, 130.1, 130.0, 129.8, 128.9, 128.5, 127.9, 127.6, 127.6, 127.2, 127.1, 126.5, 126.4, 126.1, 124.0, 123.8, 123.6, 123.5, 122.9, 121.9, 121.5, 120.9, 120.7, 120.5, 120.3, 110.2, 110.0, 109.9,109.7; MS (*m*/*z*, EI) Calcd for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub> 612.23, found: 612.20. Anal. calcd. for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>: C 86.25, H 4.61, N, 9.14; Found: C 85.88, H 4.56, N, 9.11.

**3**-(2-*Chloroquinazolin-4-yl*)-9-*phenyl-9H-carbazole* (**4**) was synthesized according to the general procedure from 2,4-dichloroquinazoline (5 g, 25 mmol) and **2** (25 mmol) in 76 % isolated yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *δ*): 8.64 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.93 (t, *J* = 7.0 Hz, 1H), 7.87 (dd, *J* = 8.5 Hz, *J* = 2.0 Hz, 1H), 7.67-7.59 (m, 5H), 7.56-7.51 (m, 2H), 7.49-7.44 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, *δ*): 170.7, 156.9, 153.1, 151.2, 143.0, 137.4, 136.7, 136.6, 135.1, 132.3, 130.2, 130.2, 129.7, 128.9, 128.2, 128.2, 127.4, 127.2, 123.9, 123.3, 121.5, 120.1, 110.6.

4-(9-Phenyl-9H-carbazol-3-yl)-2-[3-(triphenylen-2-yl)phenyl]quinazoline (CzTpQz) was synthesized according to the general procedure from **4** and **5** in 78% isolated yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.22 (s, 1H), 8.99 (s, 1H), 8.83 (d, J = 8.0 Hz, 1H), 8.80 (dd, J = 7.5 Hz, J = 2.0 Hz, 1H), 8.77 (s, 1H), 8.70 (d, J = 8.5 Hz, 1H), 8.65 (m, 3H), 8.33 (d, J = 8.5 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.05 (dd, J = 4.5 Hz, J = 1.5 Hz, 1H), 8.03 (dd, J = 4.5 Hz, J = 1.5 Hz, 1H), 7.93 (m, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.62 (m, 10H), 7.52 (tt, J = 7.0 Hz, J = 2.0 Hz, 1H), 7.47 (d, J = 3.5 Hz, 2H), 7.34 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ ): 137.4, 133.4, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.2, 129.2, 128.9, 128.6, 128.0, 127.9, 127.7, 127.5, 127.3, 127.1, 127.0, 126.6, 126.6, 123.9, 123.6, 123.5, 123.4, 123.3, 122.9, 122.1, 122.0, 120.7, 120.6, 110.2, 109.9; MS (m/z, EI) Calcd for C<sub>50</sub>H<sub>31</sub>N<sub>3</sub> 673.25, found: 673.10. Anal. calcd. for C<sub>50</sub>H<sub>31</sub>N<sub>3</sub>: C 89.13, H 4.64, N, 6.24; Found: C 89.26, H 4.58, N, 6.26.

**OLED fabrication and measurements.** OLED devices were fabricated under high vacuum (~ $10^{-4}$  Pa) chamber by thermal evaporation of organic layers onto a clean glass substrate precoated with a 150nm thick, ~ $10 \Omega$ /sq indium tin oxide (ITO) layer. Prior to use, the substrate was degreased in an ultrasonic bath by the following sequence: in detergent, de-ionized water, acetone, and isopropanol, and then cleaned in a UV-ozone chamber for 15 min. The typical deposition rates, monitored by oscillating quartz, were 0.6, 0.1, and 5.0Å/s for organic materials, lithium fluoride (LiF), and aluminum (Al), respectively. The device active area defined by the overlap between the electrodes was 9 mm<sup>2</sup> in all case. The organic layers consisted of H04 as a hole-injection and -transporting layer (HIL, HTL), TCTA as an electron-blocking and hole-transporting layer, these host materials doped with Ir(mphmq)<sub>2</sub>acac as emissive layer (EML), TPBi as an electron-transporting and hole-blocking layer, 4,7-diphenyl-1,10-phenanthroline (BPhen) as an

Keithley 2400 electrometer in dark at room temperature and only the luminance from the front face of the devices was collected with MinoltaL110 luminance meter. The electroluminescence (EL) spectra were measured with the PR650 spectrometer. All measurements were carried out immediately under ambient atmosphere without device encapsulation after the devices have been fabricated.

#### 3. RESULTS AND DISCUSSION

Synthesis and characterization. The synthetic routes of **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** were shown in **Scheme 1**. A classic and convenient Suzuki coupling reaction of 2,4-dichloroquinazoline with aryl boronic acid under suitable condition could easily produce corresponding quinazoline-centered materials. 2,4-Dichloroquinazoline reacted with 1 or 2 catalyzed by Pd(OAc)<sub>2</sub> to afford **BBIQz**, 3, 4 and **BCzQz** in 71%, 79%, 76% and 67% yields, respectively. Then 3 or 4 reacted with 5 to afford **BITpQz** or **CzTpQz** in 88% and 78% yields, respectively. **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry, and elemental analysis. These host materials were further purified by a five-zone thermal-gradient sublimator under a reduced pressure of 6 ×10<sup>-4</sup> Pa before devices fabrication.

Electrochemical and photophysical Properties. The electrochemical behaviours of BITpQz, CzTpQz, BBIQz, and BCzQz were examined by using CV and DPV, respectively, the results were listed in Table 1. Electrochemical reversibility was determined using CV, while all redox potentials were found using DPV and reported relative to a ferrocenium/ferocene (Fc<sup>+</sup>/Fc) redox couple as an internal standard.<sup>36</sup> All of the four materials displayed one or two *quasi*-reversible reduction waves with peak potentials at -1.90 ~ -2.21 V, and irreversible oxidation waves with peak potentials above 0.91 V (Figure 1, Figure S1, in supporting information). It is worth noting that CzTpQz and BCzQz showed a clear oxidation potential peak ( $E_{ox}$ )

contributed to N-phenyl-9H-carbazole moieties at 0.95 and 0.91 V respectively, and a reduction potential peak (E<sub>red</sub>) at -2.11 and -2.16 V respectively attributed to quinazoline components. However, **BITpQz** and **BBIQz** didn't show any oxidation signal in testing range of DPV due to strong electron affinities of benzoimidazole and quinazoline parts and resulted in pretty feeble irreversible oxidation waves and increasing oxidation potentials.<sup>37-38</sup> Moreover, **BITpQz** and **BBIQz** showed two *quasi*-reversible reduction waves with peak potentials at -1.92, -2.21 V and -1.9, -2.19 V respectively, which suggests that quinazoline or benzoimidazole moieties in these compounds undergo one or two electron reduction at certain potential. Comparing with **BCzQz** and **CzTpQz**, the reduction potential around -1.9 V of **BITpQz** and **BBIQz** could be assigned to the addition of benzoimidazole moiety.

UV-vis absorption, photoluminescence (PL) spectra of **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** recorded at room temperature in CH<sub>2</sub>Cl<sub>2</sub> solution and in solid film on quartz plates as well as their phosphorescent spectra in 2-Methyl-THF solution at 77K are shown in **Figure 2**, and the data were summarized in **Table 1**. The maximum absorption peaks at 337 nm for **BITpQz**, 365 nm for **CzTpQz**, 327 nm for **BBIQz**, and 341 nm for **BCzQz**, respectively can be assigned to the n– $\pi$ \* transitions, and the absorption bands under 275 nm attributed to the  $\pi$ - $\pi$ \* transition of backbone. Compared to **BBIQz** and **BITpQz**, replacement of benzoimidazole to carbazole group, red-shift absorbance were observed for both **CzTpQz** and **BCzQz** due to a donor–acceptor (D–A) greatly increasing the ICT strength and red shifts of their bands<sup>35</sup>. As expected, the absorbance bands of four compounds in thin film red-shifted substantially, 15, 8, 11, and 3 nm for **BBIQz**, **BITpQz**, **CzTpQz** and **BCzQz** respectively, probably due to the relatively intermolecular interaction in thin film. Such a phenomenon had been commonly found in other known organic materials.<sup>19</sup>

Density functional theory (DFT) calculations were performed to better understand photophysical properties and energy levels. The electron densities of the HOMO and the LUMO in vacuum state are depicted in Figure 3 by using the most popular density functional basis sets of B3LYP /6-31G\*\*. The HOMO energy level is mainly localized on carbazole units and the LUMO energy level is dispersed on quinazoline moieties for BCzQz and CzTpQz. There are two N-phenyl-9H-carbazol-3-yl groups in BCzQz, while the HOMO energy level is prefer to localize on the 9-phenyl-9H-carbazol-3-yl unit at 2-position of quinazoline. The LUMO orbitals of BBIQz and BITpQz are distributed on 4-(N-phenylbenzoimidazol-2-yl-phenyl)quinazoline parts. However, the HOMO orbital is dispersed on (N-phenylbenzoimidazol-2-yl-phenyl)quinazoline part 2-position for **BBIQz**, at and on 3-(triphenylen-2-yl)phenyl unit only for **BITpQz**, respectively, which could be contributed to the broken conjugation between triphenylene and quinazoline by meta-substitution of phenyl. Such particular feature resulted in their tunable and predictable photophysical properties.

The LUMO and the HOMO energy levels were calculated by the following equation:

HOMO (eV) = - (4.80 +  $E_{ox}$ ) or LUMO (eV) = - (4.8 +  $E_{red}$ )

HOMO (eV) = (LUMO - Eg)

Eg (eV) =  $1239.81/\lambda_{abs-onset}$ 

where  $\lambda_{abs-onset}$  (in nm) is the onset wavelength at UV-vis absorption spectra in thin solid film.<sup>39-40</sup>According to reduction potentials, the LUMO values are -2.88 eV for **BITpQz**, -2.69 eV for **CzTpQz**, -2.90 eV for **BBIQz**, and -2.64 eV for **BCzQz**, respectively. The HOMO values are -6.13 eV for **BITpQz** and -6.03 eV for **BBIQz** calculated from Eg since they didn't show any clear oxidation potentials in DPV curves. The HOMO values of **CzTpQz** (-5.75 eV from E<sub>ox</sub>, -5.78 eV from Eg ) and **BCzQz** (-5.71 eV from E<sub>ox</sub>, -5.69 eV from Eg) are estimated by using both two methods, and gave comparable data.

Interestingly, all of these compounds exhibited very similar PL spectra both in CH<sub>2</sub>Cl<sub>2</sub> solution and in thin solid film, the maximum wavelength of emission ( $\lambda_{PL}$ ) are around 450±5 nm at room temperature. Unexpectedly, emission bands of these materials in thin solid films practically remain same as those in solutions, which means that the intermolecular interactions were weak or negligible due to twisted bulky aryl groups resulting in little intermolecular electronic communication between quinazoline and aryl groups. Slight blue-shifts of  $\lambda_{PL}$  in thin solid film than those in solution could attribute to the Stokes shifts in solution. The triplet energies ( $E_T$ ) of **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** determined by peaks of the highest-energy vibronic sub-band of phosphorescent spectra in 2-methyl-THF at 77K are 2.40, 2.40, 2.46 and 2.36 eV, respectively.  $E_T$  values of them are sufficiently high to host a red phosphorescent emitters (lower than 2.1 eV) as a result of the effective prevention of reverse triplet energy transfer. Due to different feature of substituents carrying out difference of the HOMO and LUMO energy levels, they might exhibit interesting carrier-transporting properties as well as in PhOLEDs.

**Thermal Analysis.** These materials showed good thermal stabilities likely because of their high molecular weights and the rigidities of molecules. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to explore the decomposition temperature ( $T_d$ , corresponding to 5% weight loss) and glass transition temperature ( $T_g$ ) under a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup> **Figure 4**. All compounds exhibited excellent morphological and thermal stabilities in terms of their high  $T_g$  (146-154 °C) and  $T_d$  (400-447 °C) respectively. The  $T_g$  and  $T_d$  exhibit a slight increase when a benzoimidazole or carbazole was replaced by triphenylene moieties, like as **BBIQz** and **BITpQz**. In addition, no distinct crystallization and melting point were detected during heating.

To investigate the carrier-transporting properties of these materials, Carrier-transporting properties. hole-only and electron-only devices of BITpQz, CzTpQz, BBIQz, and BCzQz were fabricated. The hole only device consists of the layers ITO/host (100 nm)/MoO<sub>3</sub> (5 nm) /Al (80 nm), while the electron-only devices have the configuration of ITO/ LiF (1 nm) /host (100 nm) / LiF (1 nm) /Al (80 nm), where the LiF and Al served as a electron-injection layer and cathode. As shown in Figure 5, plots of the current density vs. applied voltage of these materials revealed different electron and hole transporting abilities. The electron mobilities of **BITpOz**, **CzTpOz**, **BBIOz**, and **BCzOz** are around 1.55×10<sup>-8</sup>, 1.35×10<sup>-9</sup>, 0.81×10<sup>-8</sup>, and  $1.58 \times 10^{-9}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, while the hole mobilities are around  $1.52 \times 10^{-11}$ ,  $1.00 \times 10^{-9}$ ,  $1.91 \times 10^{-11}$ , and  $2.82 \times 10^{-8}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively (Table 1), which were calculated by fitting the current-voltage characteristics to the space-charge limited current (SCLC) model.<sup>41</sup> The electron mobilities of **BITpOz** and **BBIQz** were about three orders of magnitude higher than their hole motilities due to the electron affinities of benzoimidazole and quinazoline units. On the other hand, when benzoimidazole moieties were replaced to N-phenylcarbazole units, CzTpQz exhibited its bipolar feature with almost same hole and electron motility. Moreover, BCzQz affords the greatest hole mobility among these materials, it was ten times higher than its electron mobility. Highly planar triphenylene moiety could usually improve carrier-transporting properties. Comparing with **BBIOz**, the electron mobility of **BITpOz** was almost twice than that of BBIQz. Similar result was observed between BCzQz and CzTpQz. However, addition of triphenylene moiety decreased the hole mobility.

**Electroluminescent properties.** To investigate the performances of **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** based PhOLEDs, several red PhOLEDs were fabricated and as well as a reference device using 4,4'-Bis(9H-carbazol-9-yl)biphenyl (CBP) as host. Ir(mphmq)<sub>2</sub>acac was chosen as the red phosphorescent

dopant since it already showed its promising saturated red emission in red PhOLEDs.<sup>42</sup> The devices were fabricated with a typical structure consisting of ITO (indium tin oxide)/H04 (60 nm)/TCTA (10 nm)/host: dopant 8 wt% (25 nm)/TPBi (10 nm)/Bphen (30 nm)/LiF (1 nm)/Al (80 nm). To improve the hole injection and transporting from the anode, H04 was spun onto the precleaned ITO substrate to form HIL and HTL. Then the electron-blocking layer consisting of a 10 nm-thick layer of TCTA<sup>43-44</sup> was implemented, due to its good transporting capability with limited intermolecular interactions in the solid states. After that, a 25 nm-thick emissive layer was evaporated, which consisted of 8 wt% phosphors doped into certain host material. To further confine the holes or generated excitons within the emissive layer, a 10 nm-thick TPBi, which possesses the low HOMO/LUMO energy levels, was used to benefit hole blocking and facilitate electron injection and transport, and a 30 nm-thick 4,7-diphenyl-1,10-phenantroline (BPhen) was selected as the electron-transport layer. LiF and Al were served as the electron-injection layer and cathode, respectively.

The performances of these devices is summarized in **Table 2**, while the relative energy levels of these materials and chemical structure of Ir(mphmq)<sub>2</sub>acac are displayed in **Figure 6**. The current density-voltage-luminance (*J-V-L*) characteristics of these devices are shown in **Figure 7**. All PhOLEDs exhibited low turn-on voltages of 2.3-3.0 V, and the corresponding current densities and luminance displayed sustained increase upon increasing driving voltage. Particularly, **BITpQz**-based OLED exhibited the lowest turn on voltage at 2.3 V, which is 0.4 V lower than that of **BBIQz**-based devices. Similarly, **CzTpQz**-based OLED showed turn on voltage at 2.5 V, which is 0.5 V lower than that of **BCzQz**-based OLED at 3.0 V as same as that of CBP-based devices. This unique feature could attribute to introduction of triphenylene group due to its planar structure resulting in higher carrier transport properties. High luminance values close to 20000 cd m<sup>-2</sup> were demonstrated at driving voltage above 9.2 V for all OLEDs.

The dramatically increased luminance and current densities indicated excellent carrier injection and transport properties of these materials, which are consistent with our design strategy of balance hole and electron densities in suitable combination zone. The external quantum efficiencies (EQE), current efficiencies (CE), and power efficiencies (PE) of these devices plotted with respect to the luminance are shown in **Figure 7**. These OLEDs achieved maximum EQE, CE, and PE of 19.2%, 18.3 cd/A, 21.7 lm/W for **BITpQz**, of 18.4%, 17.6 cd/A, 19.3lm/W for **CzTpQz**, of 15.6%, 14.4 cd/A, 16.7 lm/W for **BBIQz**, and of 17.4%, 16.7 cd/A, 15.7 lm/W for **BCzQz**, respectively, which were much higher than that of reference OLED based on CBP at 10.3%, 9.9 cd/A, 7.8 lm/W, improving over 90%.

It is well documented that the magnitude of current density under an identical voltage is not only relate to energy level of the HOMO and LUMO, but also controlled by carrier transport properties of host materials. The electroluminescence spectra of these devices are shown in **Figure 7a**. Nevertheless, a small emission band around 460 nm were observed for CBP-based OLED (**Figure 7a**, insert picture), which might contribute to exciplex emission of CBP/TPBL<sup>45</sup> Usually the electron mobility of **CBP** is much lower than its hole mobility resulting in recombination zone of **CBP**-based PhOLEDs locating the interface of host and TPBI/Bphen layer. Due to the electron affinity of quinazoline units, all other PhOLEDs based on **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** showed completion of energy transfer from hosts to dopant. The recombination zone located only in emissive layer due to their higher electron injection/transporting properties than their hole transport abilities, which is consistent with our results obtained from the hole- and electron-only devices above.

There's an interesting results shown in *J-V-L* curves that when the driving voltage was higher than 6.5 V, the current density and intensity of luminance of **CzTpQz**-based device increased dramatically and was the highest one in all devices. As we mentioned above, the electron transporting of Bphen will increase fast as

increasing of driving voltage due to effect of high electric field. **CzTpQz** with N-phenylcarbazole unit could efficiently improve hole transporting and balance carrier recombination under high operating voltage resulting in high efficiency. Similar results were demonstrated that when the driving voltage is high than 8.2 V, **BCzQz**-based device showed higher current density and intensity of luminance than those of **BBIQz**- , **BITpQz**- and **CBP**-based devices. After all, improving the electron-injection/transport abilities of host materials could ideally improve the performance of OLEDs under low operation voltage, while enhancement of hole-transporting abilities could balance the carriers to maintain high efficiency under high operating voltage. All devices also showed low efficiency roll-off at high current densities. The CE and EQE at 500 cd/m<sup>2</sup> and at 2000 cd/m<sup>2</sup> were still high as 16.9 cd/A (EQE = 17.8%) and 14.6 cd/A (EQE = 15.2%) for **BITpQz**, 16.9 cd/A (EQE = 17.8%) and 15.0 cd/A (EQE = 15.5%) for **CzTpQz**, 15.3 cd/A (EQE = 15.9 %) and 14.6 cd/A 15.0 cd/A (EQE = 13.7%) and for **BCzQz**, and 12.9 cd/A (EQE = 14%) and 11.9 cd/A (EQE = 12.6 %) for **BBIQz**, respectively. Further devices' architecture are fully expected to achieve excellent devices for applications in organic electronics.

#### 4. CONCLUSION

Four quinazoline-centered materials with benzoimidazole, carbazole, and triphenylene moieties, **BITpQz, CzTpQz, BBIQz**, and **BCzQz** were synthesized *via* a simple synthetic route. These materials exhibited outstanding morphological and thermal stabilities due to high  $T_g$  of 146-154 °C and  $T_d$  of 400-447 °C. Quinazoline unit showed the lowest reduction potential around -2.1 V, while 1-phenyl-1*H*-benzo[*d*]imidazole moiety showed the reduction potential around -1.9 V relative to Fc<sup>+</sup>/Fc. Since quinazoline system has an efficient electron affinity, further addition of electron-donating/accepting moieties could tune optoelectronic properties of its derivatives easily with electron transporting only or

bipolar nature. Highly efficient red PhOLEDs by using them as host materials were demonstrated, and achieved maximum EQE, CE, and PE of 19.2%, 18.3 cd/A, 21.7 lm/W for **BITpQz**, of 18.4%, 17.6 cd/A, 19.3lm/W for **CzTpQz**, of 15.6%, 14.4 cd/A, 16.7 lm/W for **BBIQz**, and of 17.4%, 16.7 cd/A, 15.7 lm/W for **BCzQz**, respectively, which were much higher than that of reference OLED based on CBP at 10.3%, 9.9 cd/A, 7.8 lm/W. Interestingly, **BITpQz**-based red PhOLED showed the lowest turn on voltage at 2.3 V, and the highest maximum efficiencies under low driving voltage, while **CzTpQz**-based devices exhibited higher luminescence and lower roll-off properties due to better electron/hole balance under high operating voltage. According to their tunable and promising photophysical, electrochemical and charge carrier properties, we strongly believe that these materials could give us more opportunities to achieve ideal materials for organic electronic applications.

#### **Supporting Information**

The DPV curves are shown in Figure S1. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of synthesized compounds.

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#### References

- 1 Baldo MA, Thompson ME, Forrest SR. High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer. Nature 2000;403:750-3.
- 2 Tang CW, VanSlyke SA. Organic electroluminescent diodes. Appl Phys Lett 1987;51:913-5.
- 3 Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, et al. Light-emitting diodes based on conjugated polymers. Nature 1990;347:539-41.
- 4 Lamansky S, Djurovich P, Murphy D, Abdel-Razzaq F, Lee H-E, Adachi C, et al. Highly phosphorescent bis-cyclometalated Iridium complexes: synthesis, photophysical characterization, and use in organic light emitting diodes. J Am Chem Soc 2001;123:4304-12.
- 5 Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, et al. Electroluminescence in conjugated polymers. Nature 1999;397:121-8.
- 6 Swanson SA, Wallraff GM, Chen JP, Zhang WJ, Bozano LD, Carter KR, et al. Stable and efficient fluorescent red and green dyes for external and internal conversion of blue OLED emission. Chem Mater 2003;15:2305-12.
- 7 D'Andrade BW, Forrest SR. White organic light-emitting devices for solid-state lighting. Adv Mater 2004;16:1585-95.
- 8 Huang WS, Lin JT, Chien C-H, Tao Y-T, Sun S-S, Wen Y-S. Highly phosphorescent bis-cyclometalated Iridium complexes containing benzoimidazole-based Ligands. Chem Mater 2004;16:2480-8.
- 9 Wang Q, Ma D. Management of charges and excitons for high-performance white organic light-emitting diodes. Chem Soc Rev 2010;39:2387-98.
- 10 Baldo MA, O'Brien DF, You Y, Shoustikov A, Sibley S, Thompson ME, et al. Highly efficient phosphorescentemission from organic electroluminescent devices. Nature 1998;395:151-4.
- 11 Helander MG, Wang ZB, Qiu J, Greiner MT, Puzzo DP, Liu ZW, et al. Chlorinated Indium tin oxide electrodes with high work function for organic device compatibility. Science 2011;332:944-7.
- 12 Fan C-H, Sun P, Su T-H, Cheng C-H. Host and dopant materials for idealized deep-red organic electrophosphorescence devices. Adv Mater 2011;23:2981–5.
- 13 Murawski C, Leo K, Gather MC. Efficiency roll-off in organic light-emitting diodes. Adv Mater 2013;25:6801-27.
- 14 Adachi C, Baldo MA, Forrest SR, Lammansky S, Thompson ME, Kwong RC. High-efficiency red electrophosphorescence devices. Appl Phys Lett 2001;78:1622-4.
- 15 Chen Y-M, Hung W-Y, You H-W, Chaskar A, Ting H-C, Chen H-F, et al. Carbazole–benzimidazole hybrid bipolar host materials for highly efficient green and blue phosphorescent OLEDs. J Mater Chem 2011;21:14971-8.
- 16 Su S-J, Sasabe H, Takeda T, Kido J. Pyridine-containing bipolar host materials for highly efficient blue

phosphorescent OLEDs. Chem Mater 2008;20:1691-3.

- 17 Gong S, Zhao Y, Yang C, Zhong C, Qin J, Ma D. Tuning the photophysical properties and energy levels by linking spacer and topology between the benzimidazole and carbazole units: bipolar host for highly efficient phosphorescent OLEDs. J Phys Chem C 2010;114:5193-8.
- 18 Tao Y, Wang Q, Ao L, Zhong C, Qin J, Yang C, Ma D. Molecular design of host materials based on triphenylamine/oxadiazole hybrids for excellent deep-red phosphorescent organic light-emitting diodes. J Mater Chem 2010;20:1759-65.
- 19 Chou HH, Cheng CH. A highly efficient universal bipolar host for blue, green, and red phosphorescent OLEDs. Adv Mater 2010;22:2468-71.

- 20 Su S-J, Cai C, Kido J. RGB phosphorescent organic light-emitting diodes by using host materials with heterocyclic cores: effect of nitrogen atom orientations. Chem Mater 2011;23:274-84.
- 21 Tao Y, Wang Q, Yang C, Qin J, Ma D. Managing charge balance and triplet excitons to achieve high-power-efficiency phosphorescent organic light-emitting diodes. ACS Appl Mater Interfaces. 2010;2:2813–8.
- 22 Zheng C-J, Ye J, Lo M-F, Fung M-K, Ou X-M, Zhang X-H, et al. New ambipolar hosts based on carbazole and 4,5-diazafluorene units for highly efficient blue phosphorescent OLEDs with low efficiency roll-off. Chem Mater 2012;24:643-50.
- 23 Su S-J, Cai C, Kido J. Three-carbazole-armed host materials with various cores for RGB phosphorescent organic light-emitting diodes. J Mater Chem 2012;22:3447-56.
- 24 Gong S, Chen Y, Luo J, Yang C, Zhong C, Qin J, et al. Bipolar tetraarylsilanes as universal hosts for blue, green, orange, and white electrophosphorescence with high efficiency and low efficiency roll-off. Adv Funct Mater 2011;21:1168-78.
- 25 Dong S-C, Zhang L, Liang J, Cui L-S, Li Q, Jiang Z-Q, et al. Rational design of dibenzothiophenebased host materials for PHOLEDs. J Phys Chem C 2014;118:2375–84.
- 26 Lin M-S, Chi L-C, Chang H-W, Huang Y-H, Tien K-C, Chen C-C, et al. A diarylborane-substituted carbazole as a universal bipolar host material for highly efficient electrophosphorescence devices. J Mater Chem 2012;22:870-6.
- 27 Earmme T, Ahmed E, Jenekhe S. A highly efficient phosphorescent light-emitting diodes by using an electron-transport material with high electron affinity. J Phys Chem C 2009;113:18448-50.
- 28 Tamao K, Uchida M, Izumizawa T, Furukawa K, Yamaguchi S. Silole derivatives as efficient electron transporting materials. J Am Chem Soc 1996;118:11974-5.
- 29 Hung W-Y, Chi L-C, Chen W-J, Chen Y-M, Chou S-H, Wong K-T. A new benzimidazole/carbazole hybrid bipolar material for highly efficient deep-blue electrofluorescence, yellow–green electrophosphorescence, and two-color-based white OLEDs. J Mater Chem 2010;20:10113-9.
- 30 Pan B, Wang B, Wang Y-X, Xu P, Wang L, Chen J-S, et al. A simple carbazole-N-benzimidazole bipolar host material for highly efficient blue and single layer white phosphorescent organic light-emitting diodes. J Mater Chem C 2014;2:2466-9.
- 31 Togashi K, Nomura S, Yokoyama N, Yasuda T, Adachi C. Low driving voltage characteristics of triphenylene derivatives as electron transport materials in organic light-emitting diodes. J Mater Chem 2012;22:20689-95.
- 32 Tao S, Li L, Yu J, Jiang Y, Zhou Y, Lee C-S, et al. Bipolar molecule as an excellent hole-transporter for organic-light emitting devices. Chem Mater 2009;21:1284-7.
- 33 Ye H, Chen D-C, Liu M, Su S-J, Wang Y-F, Lo C-C, et al. Pyridine-containing electron-transport materials for highly efficient blue phosphorescent OLEDs with ultralow operating voltage and reduced efficiency roll-off. Adv Funct Mater 2014;24:3268-75.
- 34 Achelle S, Rodriguez-Lopez J, Guen FR. Synthesis and photophysical studies of a series of quinazoline chromophores. J Org Chem 2014;79:7564-71.
- 35 Liu D, Zhang Z-Y, Zhang H-Y, Wang Y. A novel approach towards white photoluminescence and electroluminescence by controlled protonation of a blue fluorophore. Chem Commun 2013;49:10001-3.
- 36 Gagne RR, Koval CA, Lisensky GC. Ferrocene as an internal standard for electrochemical measurements. Inorg Chem 1980;19:2854-5.
- 37 Brunner K, Dijken AV, Bömer H, Bastiaansen J, Kiggen N, Langeveld B. Carbazole compounds as host materials for triplet emitters in organic light-emitting diodes: tuning the HOMO Level without influencing the triplet Energy in small molecules. J Am Chem Soc 2004;126:6035-42.

- 38 Ambrose JF, Carpenter LL, Nelson RF. Electrochemical and spectroscopic properties of cation radicals: III. reaction pathways of carbazolium radical ions. J Electrochem Soc 1975;122:876-94.
- 39 Xu H., Yu D-H, Liu L-L, Yan P-F, Jia L-W, Li G-M, et al. Small molecular glasses based on multiposition encapsulated phenyl benzimidazole Iridium(III) complexes: toward efficient solution-processable host-free electrophosphorescent diodes. J Phys Chem B 2010;114:141-50.
- 40 Ren S, Zeng D, Zhong H, Wang Y, Qian S, Fang Q. Star-shaped donor-π-acceptor conjugated oligomers with 1,3,5-triazine cores: convergent synthesis and multifunctional properties. J Phys Chem B 2010;114:10374-83.
- 41 Shrotriya V, Yao Y, Li G, Yang Y. Effect of self-organization in polymer/fullerene bulk heterojunctions on solar cell performance. Appl Phys Lett 2006;89:063505-1/3.
- 42 Kim DH, Cho NS, Oh H-Y, Yang JH, Jeon WS, Park JS, et al. Highly efficient red phosphorescent dopants in organic light-emitting devices. Adv Mater 2011;23:2721-6.
- 43 Su S-J, Gonmori E, Sasabe H, Kido J. Highly efficient organic blue-and white-light-emitting devices having a carrier- and exciton-confining structure for reduced efficiency roll-off. Adv Mater 2008;20:4189-94.
- 44 Lyu Y-Y, Kwak J, Jeon WS, Byun Y, Lee HS, Kim D, et al. Highly efficient red phosphorescent OLEDs based on non-conjugated silicon-cored spirobifluorene derivative doped with Ir-complexes. Adv Funct Mater 2009;19:420-7.
- 45 Zhang T, Zhao B, Chu B, Li W, Su Z, Wang L, Wang J, Jin F, Yan X, Cao Y, Wu H, Liu C, Lin T, Hou F. Blue exciplex emission and its role as a host of phosphorescent emitter. Org Electron 2015;24:1-6.

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Scheme 1. Synthesis and chemical structures of BBIQz, BITpQz, CzTpQz, and BCzQz.

Figure 1. Cyclic voltammograms of BITpQz, CzTpQz, BBIQz, and BCzQz in DMF solution

**Figure 2.** UV-vis absorption and PL spectra of **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** in CH<sub>2</sub>Cl<sub>2</sub> solutions (Abs<sub>sol</sub> and PL<sub>sol</sub>) and in neat films (Abs<sub>film</sub> and PL<sub>film</sub>) at room temperature, and phosphorescent spectra (Ph) in 2-Methyl-THF solutions at 77K.

**Figure 3.** The HOMO and LUMO levels distribution of **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** from DFT calculation

Figure 4. TGA thermograms of BITpQz, CzTpQz, BBIQz, and BCzQz. Insert: DSC thermograms

Figure 5. The current density versus voltage curves of the electron-only and hole-only devices for

#### BITpQz, CzTpQz, BBIQz, and BCzQz.

**Figure 6.** Relative energy diagram of HOMO/LUMO levels for materials used in the EL devices; Chemical structure of Ir(mphmq)<sub>2</sub>acac with HOMO/LUMO values of -5.0/-3.0 eV (dot line)

**Figure 7.** (a) EL spectra; (b) Current density-voltage-luminance (*J-V-L*) characteristics; (c) CE and PE *versus* luminance curves; (d) EQE *versus* current density curves for BBIQz, BITpQz, CzTpQz, BCzQz and CBP-based devices

 Table 1. Photophysical, Electrochemical, and Thermal properties of the BITpQz, CzTpQz, BBIQz,

 and BCzQz

 Table 2. Electroluminescence Properties of devices with BITpQz, CzTpQz, BBIQz, BCzQz, and CBP as hosts.

Table 1. Photophysical, Electrochemical, and Thermal properties of the BITpQz, CzTpQz, BBIQz, and BCzQz.

	$\lambda_{abs Sol./film}^{a}$	$\lambda_{\mathrm{PL}~\mathrm{Sol.}~/\mathrm{film}}{}^a$	$\lambda_{\mathrm{Ph}}{}^{b}$	$E_{\rm ox}/E_{\rm red}^{c}$	$E_{g}{}^{d}$	$E_T^{e}$	HOMO/LUMO	$T_{\rm g}/T_{\rm d}^{\ h}$	hole mobility <sup>g</sup>	electron mobility <sup>g</sup>
	[nm]	[nm]	[nm]	[V]	[eV]	(eV)	[eV]	[°C]	$(cm^2 v^{-1} s^{-1})$	$(cm^2 v^{-1} s^{-1})$
BITpQz	337/345	455/453	516	na/-1.92	3.246	2.40	$-6.13^{g}/-2.88^{f}$	154/425	1.52×10 <sup>-11</sup>	1.55×10 <sup>-8</sup>
CzTpQz	365/376	456/448	517	0.952/-2.11	3.092	2.40	-5.75 <sup>f</sup> /-2.69 <sup>f</sup>	153/447	1.00×10 <sup>-9</sup>	1.35×10 <sup>-9</sup>
BBIQz	327/342	455/448	505	na/-1.90	3.131	2.46	$-6.03^{g}/-2.90^{f}$	146/400	1.91×10 <sup>-11</sup>	0.81×10 <sup>-8</sup>
BCzQz	341/344	462/454	526	0.905/-2.16	3.054	2.36	-5.71 <sup><i>f</i></sup> /-2.64 <sup><i>f</i></sup>	148/438	$1.58 \times 10^{-9}$	2.82×10 <sup>-8</sup>

<sup>*a*</sup> λ<sub>abs Sol</sub>, measured in CH2Cl2; λ<sub>abs film</sub>, measured in thin solid film. <sup>*b*</sup> Measured in 2-Methyl-THF solutions at 77K <sup>*c*</sup>  $E_{ox}$  = oxidation potential;  $E_{red}$  = reduction potential; na = none appear <sup>*d*</sup> The value of  $E_g$  was calculated from the absorption onset of solid film. <sup>*e*</sup> The value of  $E_T$  was estimated from the peak values of phosphorescence spectra (λ<sub>Ph</sub>). <sup>*f*</sup> The HOMO and LUMO values were determined using the following equations:  $E_{HOMO}$  (eV) = -( $E_{ox}$  + 4.8),  $E_{LUMO}$  (eV) = - ( $E_{red}$  + 4.8); <sup>*g*</sup>  $E_{HOMO}$  (eV) =  $E_{LUMO} + E_g$ ; <sup>*h*</sup> Obtained from DSC and TGA measurements. <sup>*g*</sup> hole and electron mobilities were obtain by SCLC method.

 Table 2 Electroluminescence Properties of devices with BITpQz, CzTpQz, BBIQz, BCzQz, and CBP as hosts.

Device <sup><i>a</i></sup>	Host	$V_{\rm d}^{\ b}({\rm V})$	$L_{\max}^{c}$ (cd/m <sup>2</sup> , V)	$EQE_{max}^{c}(\%)$	$\operatorname{CE}_{\max}^{c} (\operatorname{cd} / \operatorname{A})$	$PE_{max}^{c}$ (lm/W)	$\lambda_{\max}^{d}$ (nm)
R1	BITpQz	2.3	19250, 9.2	19.2	18.3	21.7	618
R2	CzTpQz	2.5	20980, 8.2	18.4	17.6	19.3	619
R3	BBIQz	2.7	21570, 9.2	15.6	14.4	16.7	620
R4	BCzQz	3.0	19750, 8.7	17.4	16.7	15.7	618
R5	CBP	3.0	16800,9.4	10.3	9.9	7.8	618

<sup>*a*</sup> Device configuration: ITO (indium tin oxide)/H04 (60 nm)/TCTA (10 nm)/host: dopant 8 wt% (25 nm)/TPBi (10 nm)/Bphen (30 nm)/LiF (1 nm)/Al (80 nm). <sup>*b*</sup> V<sub>d</sub>: the operating voltage at a brightness of 1 cd m<sup>-2</sup>. <sup>*c*</sup>  $L_{max}$ : maximum luminance; EQE<sub>max</sub>: maximum external quantum efficiency; CE<sub>max</sub>: maximum current efficiency; PE<sub>max</sub>: maximum power efficiency. <sup>*d*</sup>  $\lambda_{max}$ : the wavelength where the EL spectrum has the maximum intensity.

![](_page_25_Figure_1.jpeg)

Suzuki condition:  $Pd(OAc)_2/PPh_3/K_2CO_3$ , 1,4-dioxane/H<sub>2</sub>O

Scheme 1. Synthesis and chemical structures of BBIQz, BITpQz, CzTpQz, and BCzQz.

![](_page_26_Figure_1.jpeg)

Figure 1. Cyclic voltammograms of BITpQz, CzTpQz, BBIQz, and BCzQz in DMF solution.

![](_page_27_Figure_1.jpeg)

**Figure 2.** UV-vis absorption and PL spectra of **BITpQz**, **CzTpQz**, **BBIQz**, and **BCzQz** in  $CH_2Cl_2$  solutions (Abs<sub>sol</sub> and PL<sub>sol</sub>) and in neat films (Abs<sub>film</sub> and PL<sub>film</sub>) at room temperature, and phosphorescent spectra (Ph) in 2-Methyl-THF solutions at 77K.

![](_page_28_Figure_1.jpeg)

Figure 3. The HOMO and LUMO levels distribution of BITpQz, CzTpQz, BBIQz, and BCzQz from DFT calculation

![](_page_29_Figure_1.jpeg)

Figure 4. TGA thermograms of BITpQz, CzTpQz, BBIQz, and BCzQz. Insert: DSC thermograms

![](_page_30_Figure_1.jpeg)

Figure 5. The current density *versus* voltage curves of the electron-only and hole-only devices for BITpQz, CzTpQz, BBIQz, and BCzQz.

![](_page_31_Figure_1.jpeg)

**Figure 6.** Relative energy diagram of HOMO/LUMO levels for materials used in the EL devices; chemical structure of Ir(mphmq)2acac with HOMO/LUMO values of -5.0/-3.0 eV (dot line)

![](_page_31_Figure_3.jpeg)

![](_page_32_Figure_1.jpeg)

**Figure 7.** (a) EL spectra; (b) Current density-voltage-luminance (*J-V-L*) characteristics; (c) CE and PE *versus* luminance curves; (d) EQE *versus* current density curves for BBIQz, BITpQz, CzTpQz, BCzQz and CBP-based devices

## Highlights

2,4-Substituted-Quinazoline dyes were synthesized and characterized.

DFT calculation, electrochemical, and photophysical properties were discussed.

Efficient red PhOLEDs with low turn-on voltage were demonstrated by using them as host materials.

Bipolar or electron-only host materials showed potential utilizations in efficient PhOLEDs.

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