Rational design of quinoxaline-based bipolar host materials for highly efficient red phosphorescent organic light-emitting diodes†

Zilong Feng,‡a Zhixiang Gao,‡b Wenshan Qu,*b Tingting Yang,†b Jiangang Li†b and Lixiong Wang*a

Two novel bipolar carbazole/diphenylquinoxaline-based host materials 3-(2,3-diphenylquinoxalin-6-yl)-9-phenyl-9H-carbazole (M1) and 3-(2,3-diphenylquinoxalin-6-yl)phenyl)-9-phenyl-9H-carbazole (M2) have been rationally designed and synthesized. The phenyl spacer between the functionalized quinoxaline moiety and the carbazole moiety is also introduced to investigate its influence on their photophysical properties. The chemical structures, thermal, photophysical and electrochemical properties of the two host materials were characterized and explored in detail. Red phosphorescent light-emitting diodes with M1 and M2 as hosts were prepared to explore their electroluminescent properties. Both M1 and M2 host-based red devices exhibit outstanding electroluminescent performance. For example, two red devices all realize good red emission with the maximum at 594 nm, the maximum external quantum efficiency and luminance can reach 14.66% and 28 619 cd m⁻² for M1-based devices and 15.07% and 28 818 cd m⁻² for M2-based devices, indicating compounds M1 and M2 designed in this work have potential applications in the development of high-performance monochrome and white OLEDs.

The red emission component is an integral part of both high-quality solid state lightings and displays. 33–39 The performance of red phosphorescent OLEDs is not determined by phosphors themselves, but also closely related to the host materials. Bipolar host materials that could balance the carrier-transportations for improving the efficiency of phosphorescent OLEDs have become the current research focus. Many bipolar host materials have been explored in highly efficient red phosphorescent OLEDs, especially in the design of acceptor moieties. 40–42 Recently, diphenylquinoxaline derivatives showing excellent electron-transportation property also have been selected as the novel acceptor moiety to realize the bipolar host materials. 33,34 For instance, Cheng et al. designed an excellent bipolar host material which is composed of two 6H-indolo[2,3-b]quinoxaline unit bridged by the tetraphenylsilane core realizing high-efficiency red phosphorescent OLEDs. 35 It is still necessary to further explore the quinoxaline-based bipolar host materials.

Herein, we designed two novel host materials (M1 and M2) by combining the quinoxaline moiety and carbazole moiety, with various linkage ways between carbazole and quinoxaline moiety. Red phosphorescent OLEDs with M1 and M2 as hosts were successfully fabricated, and both M1 and M2 hosts-based red devices exhibit the outstanding electroluminescent performance. For example, the maximum external quantum efficiency (EQE) and luminance reach 14.66% and 28 619 cd m⁻² for M1-
based red device, 15.07% and 28 818 cd m\(^{-2}\) for M2-based red device.

**Experimental**

**General experimental information**

The detailed information on the solvents, chemicals, and general experiments can be found in the ESI.†

**Synthesis of bipolar host materials**

The synthesis of 3-(2,3-diphenylquinoxalin-6-yl)-9-phenyl-9H-carbazole (M1). 3-Bromo-9-phenyl-9H-carbazole (1.5 g, 4.7 mmol), 2,3-diphenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoxaline (1.9 g, 4.7 mmol), K\(_2\)CO\(_3\) (1.4 g, 10 mmol), 2,3-diphenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoxaline (1.9 g, 4.7 mmol), K\(_2\)CO\(_3\) (1.4 g, 10 mmol), tetrakis(triphenylphosphine)palladium (50 mg) and H\(_2\)O (15 mL) were dissolved in THF (50 mL). The mixture was allowed to reflux for 18 h. After the reaction completed, the mixture was cooled, then extracted with methylene chloride, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated. The crude mixture was cooled, then extracted with methylene chloride, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated. The crude product was purified by column chromatography (petroleum ether: dichloromethane = 2:1) to obtain a solid powder (yield 81%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.60 \text{ (d, } J = 1.60 \text{ Hz, 1H), 8.53 \text{ (d, } J = 1.60 \text{ Hz, 1H), 8.29–8.82 \text{ (m, 3H), 7.88 \text{ (dd, } J = 8.40, 2.00 \text{ Hz, 1H), 7.67–7.61 \text{ (m, 4H), 7.58–7.49 \text{ (m, 6H), 7.47–7.44 \text{ (m, 2H), 7.39–7.33 \text{ (m, 7H). 13C NMR} \text{ (101 MHz, CDCl3) } \delta = 153.75, 152.83, 143.62, 141.51, 141.50, 140.93, 140.27, 139.01, 138.98, 137.48, 131.68, 130.18, 130.02, 129.92, 129.90, 129.35, 128.91, 128.85, 128.33, 128.32, 127.73, 127.12, 126.42, 125.92, 125.60, 124.17, 123.40, 120.41, 119.36, 110.44, 110.08. HRMS (ESI, \(m/z\)): [M + H\(^+\)] \text{ calcd for C}_{38}\text{H}_{25}\text{N}_3, 524.2127, found 524.2133. Anal. calcd for C\(_{38}\)H\(_{25}\)N\(_3\): C 87.16, H 4.81, N 8.02; found: C 87.12, H 4.90, N 8.09.}

**Scheme 1** The synthetic routes of bipolar host materials M1 and M2.
Result and discussion

Synthesis and characterization

The detailed synthetic routes and chemical structures of bipolar host materials are shown in Scheme 1. The synthesis of M1 and M2 was realized through Suzuki coupling reaction by reacting 3-bromo-9-phenyl-9H-carbazole or 3-(4-bromo-phenyl)-9-phenyl-9H-carbazole with 2,3-diphenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoxaline, respectively in high yields (over 75%). Both two compounds were confirmed by high-resolution mass spectra and nuclear magnetic resonance spectra (shown in ESI†). Under a nitrogen atmosphere, using the TGA and DSC to characterize the thermal properties of compounds M1 and M2. As shown in Fig. 1 and Table 1, the onset decomposition temperature (T_d) corresponding to 5% weight loss) according to the TGA data is 321 °C for M1 and is 415 °C for M2. We obviously found that the endothermic glass transition temperature (T_g) for M1 and M2 is determined to be 176 °C and 218 °C by analyzing the DSC traces, indicating M1 and M2 compounds are suitable for developing OLEDs by thermal evaporation technology. Owing to its much more steric structure of the molecule, the host M2 shows obviously both high T_g and T_d values. The relatively high thermal stabilities of the host materials are benefit for improving the morphology of the film and lifetime of the device by suppressing the phase separation and crystallization during the operation process of device.

Photophysical properties

The absorption and emission properties of M1 and M2 were investigated in toluene. As depicted in Fig. 2a, the absorption of M1 and M2 exhibits bands in the range from 250 to 430 nm (247, 298, 387 nm for M1; 254, 303, 378 nm for M2), attributed to the π–π* electronic transition of the quinoxaline and carbazole unit.5,14,40–42 M1 and M2 show almost the same absorption spectra in spite of the larger π-electron conjugation of compound M2, implying that the introduction of the phenyl spacer almost has little effect on the absorption properties of these donor–acceptor systems.

However, quite different from their absorption properties, two compounds exhibited the different maximum emission wavelength (λ_max = 493 nm for M1; λ_max = 518 nm for M2) in toluene at room temperature, as depicted in Fig. 2a and Table 1. The slight red shifted in the emission of M2 could be attributed to the larger π-electron conjugation. The compounds M1 and M2 exhibited sky-blue or green fluorescence with energy gap of 2.51 and 2.39 eV in toluene, implying that the π-electron conjugation and co-planarity of molecule have been tuned by the phenyl spacer between functionalized quinoxaline moiety and carbazole moiety. In addition, the low temperature phosphorescence spectra of the compound M1 and M2 were also recorded at 77 K to calculate the triplet energies. As shown in the Fig. 2b, the low temperature phosphorescence spectra of both compounds were almost the same. The maximum emission of the phosphorescence spectra was at the wavelength of 553 nm. The triplet energy levels were calculated by the first emission peak of the low-temperature phosphorescence spectra

Fig. 1  The thermogravimetric (a) and differential scanning calorimetry (b) analysis of bipolar host materials M1 and M2.

| Table 1  Photophysical properties of the bipolar host materials M1 and M2 |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Compound | λ_{abs}/λ_{onset} [nm] | λ_{max} [nm] | λ_{phos} [nm] | E_g [eV] | E_f [eV] | E_{onset} [V] | HOMO [eV] | LUMO [eV] | T_d [°C] | T_g [°C] |
| M1 | 247, 298, 387 | 493 | 553 | 2.51 | 2.24 | 1.20 | −5.60 | −3.09 | 321 | 176 |
| M2 | 254, 303, 378 | 518 | 2.39 | 2.24 | 1.20 | 1.20 | −5.60 | −3.21 | 415 | 218 |

*a Measured in toluene at room temperature. b Measured in toluene at 77 K. c Calculated by the equation E_g = 1240/λ_{max}. d Calculated by the first peak of phosphorescence spectra measured at 77 K, E_f = 1240/λ_{phos}. e Calculated by the equation E_{HOMO} = −4.4 − E_{onset}. f Calculated by the equation E_{LUMO} = E_{HOMO} + E_g. g Measured by TGA. h Measured by DSC.
and were determined to be 2.24 eV, which is suitable for the red OLEDs.\(^{24}\) In addition, at the 77 K, we can observe the electronic transitions between the \(T_1\) substates (substates III, II, I) and the ground state \(S_0\). From the intensity distribution, it can be concluded that the radiative transition from the lowest substate I to the ground state \(S_0\) is largely forbidden, while the transitions from the two higher-lying substates III and II to the ground state are significantly more allowed.

Electrochemical properties

As depicted in Fig. 3, using a standard three-electrode electrochemical cell in an electrolyte solution, the electrochemical behavior of compounds M1 and M2 was investigated by cyclic voltammetry. The energy level of the highest occupied molecular orbital (HOMO) for M1 and M2 were calculated to be both \(-5.60\) eV from the onset potentials of oxidation peak, while the energy level of the lowest unoccupied molecular orbital (LUMO) of these host materials were determined to be \(-3.09\) and \(-3.21\) eV according to the band gap energy (\(E_g\)) and HOMO energy level. The data of \(E_g\) and HOMO/LUMO energy levels were listed in Table 1. The same HOMO levels of both compounds can be explained by sharing the same electron-donor carbazole group, which indicated that the phenyl spacer between the functionalized quinoxaline moiety and carbazole moiety has no effect on the HOMO levels. However, the LUMO energy of compound M1 (\(-3.09\) eV) were higher than that of M2 (\(-3.21\) eV), implying that the phenyl spacer have evident influence on the LUMO of these donor–acceptor systems.\(^{40-42}\)

Red phosphorescent OLEDs

Considering the triplet energy levels (2.24 eV) of M1 and M2 is suitable for red OLEDs, to order to prove their potential application in OLEDs, two doped device of ITO/40 nm-poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer/45 nm-di-(4-(N,N-di-p-tolyl-amino)-phenyl)cyclohexane (TAPC) layer/5 nm-4,4’,4”-tris(carbazol-9-yl)triphenylamine (TCTA) layer/20 nm-hosts: 5% wt bis(2-phenylquinolinato)-acetylacetonate iridium(III) (Ir(pq)\(_2\)acac) layer/55 nm-1,3,5-tri((3-pyridyl)-phen-3-yl)benzene (TmPyPB) layer/0.8 nm-lithium fluoride (LiF) layer/80 nm-aluminum (Al) layer were fabricated by vacuum thermal deposition, where hosts are M1 and M2, corresponding to the device R1 and R2, respectively. The device structure and organic molecules used in device fabrication are displayed in Fig. 4. In two red devices, different function materials were chosen on the basis of knowing the energy level of materials, and the thickness of different layers was decided by combining the reported relevant literature and mobility of materials.\(^{46,25}\) In these devices, ITO was used as an anode; the LiF/Al layers were employed as a composite cathode; 40 nm-thick PEDOT:PSS layer was used as the hole-injection layer; 45 nm-thick TAPC layer was used as the hole-transporting layer; 5 nm-thick TCTA layer was used as the exciton blocking layer and 55 nm-thick TmPyPB layer as the electron transport layer. From the energy level diagram of two red devices in Fig. S1 in ESI,\(^{\dagger}\) we can see that TCTA and TmPyPB can
Fig. 4. The device structure of red devices and organic molecules used in device fabrication.

Fig. 5. Normalized EL spectra and CIE coordinates at 6 V (a), J−V−L (b), CE−J (c), and PE−L (d) characteristic curves for the M1- and M2-based red devices.
Ir(pq)₂acac. Meanwhile, from Fig. S2 in ESI, 0.389) for 594 nm, and CIE coordinates are (0.575, 0.391) and (0.576, 0.389) are almost completely overlapping with the same peak at 594 nm, and CIE coordinates are (0.575, 0.391) and (0.576, 0.389) for M₁- and M₂-based devices, respectively. These are well consistent to the emission characteristic of emitter Ir(pq)₂acac. Meanwhile, from Fig. S2 in ESI, it is found that there is almost no EL color shift vary at a wide voltage range of 5–8 V for two red devices, which indicates (i) the carrier recombination zone and exciton are well confined in the red EML; and the energy in M₁ and M₂ hosts can be effectively transferred to Ir(pq)₂acac when Ir(pq)₂acac is doped in M₁ and M₂ hosts for two red device. The above result preliminarily proved the feasibility of compounds M₁ and M₂.

Fig. 5a depicts the normalized EL spectra of M₁- and M₂-based devices at a voltage of 6 V. Clearly, both M₁- and M₂-based devices emit red light, and the EL spectra for two devices are almost completely overlapping with the same peak at 594 nm, and CIE coordinates are (0.575, 0.391) and (0.576, 0.389) for M₁- and M₂-based devices, respectively. These are well consistent to the emission characteristic of emitter Ir(pq)₂acac. Meanwhile, from Fig. S2 in ESI, it is found that there is almost no EL color shift vary at a wide voltage range of 5–8 V for two red devices, which indicates (i) the carrier recombination zone and exciton are well confined in the red EML; and the energy in M₁ and M₂ hosts can be effectively transferred to Ir(pq)₂acac when Ir(pq)₂acac is doped in M₁ and M₂ hosts for two red device. The above result preliminarily proved the feasibility of compounds M₁ and M₂ as hosts for red OLEDs.

In fact, the high EL performance for both M₁- and M₂-based devices further demonstrate that both M₁ and M₂ are excellent host materials for red phosphorescent OLEDs. For example, as shown in Fig. 5b, both M₁- and M₂-based devices show a relatively low turn-on voltage of 3.6 V, and all achieve very high maximum luminance of 28 619 cd m⁻² for device R₁ and 28 818 cd m⁻² for device R₂. From Fig. 5c, d and S3 in ESI,† both M₁- and M₂-based devices achieve high device efficiency, and the maximum current efficiency (CE), power efficiency (PE), and EQE reach 28.57 cd A⁻¹, 19.95 lm W⁻¹, and 14.66% for M₁-based red device and 29.29 cd A⁻¹, 20.45 lm W⁻¹, and 15.07% for M₂-based red device. All above results indicate that these diphenylquinoxaline-based bipolar host materials have potential applications for the development of high-performance red OLEDs. In addition, the performance of red OLEDs in this work are much higher than that in the reported results (PE = 20.45 lm W⁻¹, CE = 29.29 cd A⁻¹, EQE = 15.07% vs. PE = 15.4 lm W⁻¹, CE = 21.9 cd A⁻¹, EQE = 12.2%) showing in Fig. S4,† indicating that the connection ways of electron acceptor/donor moieties have great influence on performance of the host materials (Table 2).

**Conclusion**
To conclude, two novel quinoxaline-based bipolar host materials have been rational design and prepared successfully via the Suzuki coupling reaction in high yields for application in red phosphorescent OLEDs. By incorporating the diphenylquinoxaline and carbazole unit as the electron donor and acceptor, meanwhile, the phenyl spacer between the functionalized quinoxaline moiety and carbazole moiety is also introduced to investigate its influence on their photophysical properties. Their thermal, photophysical and electrochemical properties were investigated and discussed in details. The red phosphorescent OLEDs with M₁ and M₂ as host were fabricated, and it is found both M₁ and M₂ hosts-based red devices exhibit the outstanding electroluminescent performance. For example, two red devices all realize good red emission with peak at 594 nm, and the maximum luminance and external quantum efficiency reach 28 619 cd m⁻² and 14.66% for M₁-based device and 28 818 cd m⁻² and 15.07% for M₂-based device, indicating that compounds M₁ and M₂ synthesized in this work have the potential applications in the development of high performance red and white OLEDs.

**Conflicts of interest**
There are no conflicts to declare.

**Acknowledgements**
Zilong Feng and Zhixiang Gao contributed equally to this work. The authors are grateful for the financial support of the National Natural Science Foundation of China (21872088, 11874245), Shanxi Province Science and Technology Key Project (201703D121037-2), Datong City Science and Technology Research Project (2018018).

**References**

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**Table 2** The EL performance parameter summary for M₁- and M₂-based devices

<table>
<thead>
<tr>
<th>Device</th>
<th>Host</th>
<th>Voltage (V)</th>
<th>CE [cd A⁻¹]</th>
<th>PE [lm W⁻¹]</th>
<th>EQE [%]</th>
<th>L (cd m⁻²)</th>
<th>CIE [x, y]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>M₁</td>
<td>3.6</td>
<td>28.57</td>
<td>19.95</td>
<td>14.66</td>
<td>28 619</td>
<td>(0.575, 0.391)</td>
</tr>
<tr>
<td>R2</td>
<td>M₂</td>
<td>3.6</td>
<td>29.29</td>
<td>20.45</td>
<td>15.07</td>
<td>28 818</td>
<td>(0.576, 0.389)</td>
</tr>
</tbody>
</table>

*a Voltage at a luminance of >1 cd m⁻². *b L is the abbreviation of luminance. *c Measured from the EL spectra at 6 V.*