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## Quinoxaline and Pyrido[x,y-b]pyrazine Based Emitters: Tuning Normal Fluorescence to Thermally Activated Delayed Fluorescence and Emitting Color Over Entire Visible Light Range

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**Abstract**: Quinoxaline (Q), pyrido[2,3-b]pyrazine (PP) and pyrido[3,4-b]pyrazine (*i*PP) are used as electron acceptors (A) to design a series of D- $\pi$ -A type light-emitting materials with different donor (D) groups. By adjusting the molecular torsion angles through changing donor from carbazole (Cz) to 10-dimethyl-acridine (DMAC) or 10H-phenoxazine (PXZ) for a fixed acceptor, the luminescence is tuned from normal fluorescence to thermally activated delayed fluorescence (TADF). By gradually enhancing the intramolecular charge transfer extent through combining different D and A, the emission color is continuously and regularly tuned from pure blue to orange-red. Organic light-emitting diodes (OLEDs) containing these compounds as doped emitter exhibit bright electroluminescence with emission color covering the entire visible light range. An external quantum efficiency ( $\eta_{ext}$ ) of 1.2% with excellent color coordinates of (0.16, 0.07) is obtained for the pure blue OLED of Q-Cz. High

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 $\eta_{\text{ext}}$ s of 12.9% (35.9 cd A<sup>-1</sup>) to 16.7% (51.9 cd A<sup>-1</sup>) are realized in the green, yellow and orange-red TADF-OLEDs. All the PP and *i*PP based TADF emitters exhibit superior efficiency stabilities to the quinoxaline analogues. It provides a practical strategy to tune the emission color of quinoxaline and pyrido[x,y-b]pyrazine derivatives with same molecular skeletons over the entire visible light range.

**Keywords**: thermally activated delayed fluorescence (TADF), quinoxaline, pyrido[2,3-b]pyrazine, entire visible light range, organic light-emitting diodes (OLEDs)

#### Introduction

As the third-generation organic light-emititing diodes (OLED) emitters, thermally activated delayed fluorescence (TADF) mateirals have attracted more and more attentions due to advantageous merits of high emission efficiency and low cost.<sup>1.2</sup> It is required that the energy splitting between  $S_1$  and  $T_1$  ( $\Delta E_{ST}$ ) should be as small as possible to decrease the exchange interaction integral of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) wave functions of a molecule and to guarantee efficient reverse intersystem crossing (RISC) of  $T_1$  with thermal activation into  $S_1$  and the subsequent delayed fluorescence.<sup>3,4</sup> Accordingly HOMO and LUMO should be spatially separated. In most cases highly twisted molecular configuration is necessary to enhance the HOMO/LUMO separation and facilitate the TADF feature. When TADF materials are used as the emitting component of OLEDs, all the electrogenerated triplet excitons formed on TADF molecules (that occupying 75% of all the excitons generated through charge recombination) are possible to be upconverted into singlet excitons and emit delayed fluorescence, and all the electrogenerated singlet excitons of TADF emitter (that occupying 25% of all the electrogenerated excitons) can emit prompt fluorescence in a certain fluorescence quantum yield. In this way, all the electrogenerated singlet and triplet excitons can be harvested for light emission and a theoretical uplimit of unity for internal quantum efficiency (IQE) can be achieved in TADF-OLEDs.<sup>5,6</sup> Obviously the same electroluminescence (EL) performance as phosphorescent OLEDs can be achieved by using the pure organic TADF emitters without involving the noble metal phosphors. Since the pioneering report of TADF-OLEDs by Adachi and coworkers,<sup>7</sup> have always been the hotspot in OLED research field. In recent years, a great many efficient TADF emitters have been developed based on various type of electron acceptor units such as triazine,<sup>8</sup> sulfone,<sup>9</sup> benzophenone,<sup>10,11</sup> pyrimidines,<sup>12</sup> quinoxaline,<sup>13,14</sup> and so forth, leading the OLEDs research field stepping into a new stage of diversity in light-emitting materials.

TADF molecules are typically characterized by the donor- $\pi$ -acceptor (D- $\pi$ -A) or D-A architectures, in which the weak intramolecular charge transfer between D and A determines the S<sub>1</sub> and T<sub>1</sub> excited state energies of the molecule. Apparently TADF molecules of different emission colors or even covering the whole visible light range can be constructed by combinating different D and A and by adjusting the steric molecular conformations. Wong and coworkers reported a series of TADF emitters using 9,9'-dimethylacridan (DMAC) as common donor. The emission wavelengths were widely tunable from deep blue to yellow not only by the general acceptor

strength due to the characters of heteroarene and CN-substitution pattern but also by the subtle control of in-acceptor conformation (twist angles). Highly efficient blue-green to yellow TADF-OLEDs having external quantum efficiencies (EQE,  $\eta_{ext}$ ) of up to 23.1%–31.3% were achieved using these efficient TADF emitters.<sup>15</sup> Yasuda and coworkers built a group of full-color TADF molecules comprising a central phthalonitrile or 2,3-dicyanopyrazine acceptor core coupled with various donor units of different electron-donating abilities, which exhibited the moderate to high  $\eta_{ext}$ s of 8.7%, 18.9%, 13.3% in blue, green and orange-red OLEDs, respectively.<sup>16</sup> Wang and coworkers tuned the emission color from yellow to red for a group of 2,3-dicyanopyrazinophenanthrene (DCPP) based TADF emitters by varying the electron donor from Cz, via diphenylamine (DPA), to DMAC. Moderate  $\eta_{ext}$  of 10.1% to 16.9% were obtained for those yellow to red TADF-OLEDs.<sup>17</sup> The same acceptors coupled with different donors may result in different luminescence mechanisms. For example, even based on the identical D- $\pi$ -A structural strategy, the molecule incorporating carbazole as a mild electron-donor and sulfone as an electron-acceptor (CzS2) is a normal fluorescent compound and exhibited a maximum  $\eta_{\text{ext}}$  of 2.7% in OLED,<sup>18</sup> while the analogue containing DMAC as donor and one diphenylsulfone (DPS) acceptor (DMAC-DPS) revealed TADF feature and achieved a maximum  $\eta_{ext}$  of 19.5% in corresponding OLED.<sup>19</sup> The small molecular D–A or D- $\pi$ -A chromophores of various colors have achieved good performance so far, and considerable progresses have been made in  $\eta_{ext}$ s of RGB TADF OLEDs, e.g. nearly 37% for sky-blue,<sup>20</sup> over 30% for green<sup>21</sup> and 21-29.2% for orange-red.<sup>22</sup> As far as we

know, these values should be the state-of-art efficiency for each primary color TADF OLEDs reported so far. It is clear that the electroluminescent properties of individual RGB emitting TADF materials are efficient and stable and have been successfully utilized in OLEDs. However, the TADF materials of similar molecular skeletons with emission covering the wide or entire visible light range have been rarely reported so far. In addition, it can be found that many orange-red TADF emitters have played positive roles in both sinlge-color and white OLEDs, however, only a few materials can achieve high efficiency.<sup>23</sup> This is partially because the long-wavelength emitters (orange to red) are generally subjected to the increasing non-radiative internal conversion process governed by the energy gap law, and then resulting in low photoluminescence quantum yield (PLQYs,  $\Phi_{PL}$ ).<sup>24</sup> Furthermore, efficiency roll-off at high driving range is also a concerned issue for orange-red TADF-OLEDs. There is a design regulation that most of the reported TADF emitters adopt a twisted intramolecular charge-transfer (ICT) configuration, in which the electron donor and acceptor units are incorporated to be orthogonal to each other.<sup>25</sup> Therefore, high rigidity and strong charge transfer (CT) states in D-A systems are desired for constructing efficient orange-to-red TADF emitters.

With the development and evolution of D-A or D- $\pi$ -A type TADF molecules, the challenge is to rationally design novel emitters based on simple versatile molecular scaffolds. Quinoxaline (Q) and pyrido[x,y-b]pyrazine have the same double hexatomic ring aromatic frameworks despite the only difference that pyrido[x,y-b]pyrazine has one nitrogen atom replacing one carbon atom of

quinoxaline ring. It can be expected that the introduction of the additional  $sp^2$  type N atom in pyrido[x,y-b]pyrazine will definitely enhance the electron-withdrawing ability in comparison with quinoxaline. In addition, with the different location of the pyridine ring, pyrido[2,3-b]pyrazine (PP) exhibits Ν atom in stronger electron-deficient ability than its isomer pyrido[3,4-b]pyrazine (*iPP*). Quinoxaline has been explored as electron acceptor to build TADF molecules,<sup>26,27</sup> while there is few report utilizing pyrido[2,3-b]pyrazine or pyrido[3,4-b]pyrazine as acceptor units to construct TADF emitters. Based on the stepwise enhancement of the electron-withdrawing ability in the order of Q, iPP, and PP, it can be expected that continuous color tuning can be realized if these acceptors are used to build fluorophors by simultaneously adjusting the electron donating ability of the donor groups. Herein, we designed and prepared a series of novel D- $\pi$ -A type fluorescent emitters using Q, *iPP*, and PP as electron acceptors and central linking bridges, and carbazole (Cz) 9,10-dimethyl-acridine (DMAC) and 10H-phenoxazine (PXZ) as the electron donors. Double donor groups were linked to each central acceptor bridge to form the wedge-shaped molecules Q-Cz, Q-DMAC, iPP-DMAC, PP-DMAC, *i*PP-PXZ and PP-PXZ (Scheme 1). The photophysical, electrochemical, and thermal properties of these compounds were systematically studied. It was observed that, despite the similar acceptor skeleton and same  $D-\pi-A-\pi-D$  configuration and wedgeshape in all these molecules, the carbazole based Q-Cz is the normal fluorescent compound, while the other five analogues show typical TADF feature, which is attributed to the less crowded steric feature of carbazole ring than other

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donor groups. In virtue of continuous regulation of both acceptor strength and donor strength, the emission wavelengths of these six analogues were successfully tunable from pure blue via green to orange-red. These emitters were used to fabricate OLEDs and electroluminescence with continuously tunable color from blue to orange-red was obtained. Moderate to high efficiencies of 1.2%, 16.7%, 14.1% and 13.0% were achieved for the pure blue, green, yellow, and orange-red OLEDs. It provides a practical strategy using quinoxaline and pyrido[x,y-b]pyrazine to construct simple molecules to realize continuous tuning of emission color from pure blue to orange red. This is the first journal report to use pyrido[2,3-b]pyrazine and pyrido[3,4-b]pyrazine as acceptor units to construct TADF emitters.



**Scheme 1**. Structures of the quinoxaline and pyrido[x,y-b]pyrazine based RGB TADF emitters.

#### **Results and Discussion**

| Synthesis         | and Thermal         | Properties. Th         | e structur            | e and de    | tailed s  | ynthetic           |
|-------------------|---------------------|------------------------|-----------------------|-------------|-----------|--------------------|
| procedures of     | all compounds a     | re described i         | n Scheme              | 1 and S     | cheme     | S1. The            |
| important         | intermediate        | s 2,3                  | 3-dichloroq           | uinoxaline  |           | $(a),^{28}$        |
| (4-(9H-fluoren-   | -9-yl)phenyl)boror  | nic                    | acio                  | d           |           | (b), <sup>29</sup> |
| 1,2-bis(4-brom    | ophenyl)ethane-1,2  | 2-dione (c), $^{30}$ 2 | ,3-bis(4-bro          | omophenyl   | )quinox   | aline (d),         |
| 2,3-bis (4-       | -bromophenyl)       | pyrido [3              | 3,4-b]                | pyrazine    | (e)       | and                |
| 2,3-bis(4-brom    | ophenyl)pyrido[2,2  | 3-b]pyrazine (i        | f) <sup>31</sup> were | synthesize  | ed accor  | ding to            |
| previously repo   | orted methods. The  | e carbazole base       | ed compour            | nd Q-Cz w   | as then j | prepared           |
| in high yield b   | by Suzuki cross-co  | upling reaction        | of interme            | ediates a a | und b. T  | he other           |
| five analogues    | were synthesized    | via Buchwald           | -Hartwig r            | eaction of  | d, e, o   | r f with           |
| 9,9-dimethylac    | eridan (DMAC-H)     | or 10H-phenox          | azine (PXZ            | Z-H) at mo  | oderate y | yields of          |
| 40-50%. The c     | details of synthesi | s and character        | rization for          | all these   | compou    | unds are           |
| illustrated in su | apporting informati | on.                    |                       |             |           |                    |

The thermal and morphological properties of these compounds were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere, the corresponding data are summarized in Table 1. As shown by TGA thermograms in Figure S1, most of these compounds show high decomposition temperatures ( $T_d$ , corresponding to 5% weight loss) over 400 °C, indicating excellent thermal stabilities. While PP-PXZ exceptionally starts to decompose at 164 °C. During the second heating cycle in the DSC measurement

(Figure 1), Q-DMAC, PP-DMAC and *i*PP-PXZ were found to show high glass transition temperatures ( $T_g$ ) of 124 °C, 137 °C and 131 °C, respectively. No glass transition was observed for Q-Cz and *i*PP-DMAC under the present measurement conditions. PP-PXZ was not explored for DSC measurement due to easy decomposition in low temperature range. The high  $T_d$  and  $T_g$  indicate that emitters have good thermal and morphological stability, which should be attributed to their relatively high molecular weights and appropriate molecular conformations and be favorable for good device stability when used in OLEDs.



Figure 1. DSC traces (second heating cycle) of compounds recorded under nitrogen at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>.

Steady-State Photophysical Properties. The steady-state photophysical properties of these compounds were analyzed using UV-vis absorption and photoluminescence (PL) spectra in dilute toluene solutions. As shown by the absorption spectra in Figure 2a, Q-Cz shows different absorption features with other analogues. The strong and moderate absorption bands below 350 nm for Q-Cz should be assigned to the characteristic  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions of carbazole and

quinoxaline rings.<sup>32,33</sup> The additional absorption band at about 370 nm should originate from the intramolecular charge transfer (ICT) transition from electron-donating carbazole to the electron-deficient quinoxaline moieties. For three DMAC-based compounds, the strong absorption bands at about 280 nm and moderate bands at 345 nm should be due to the intrinsic electron transitions of acridine and acceptor parts (pyrido[x,y-b]pyrazine), while the weak absorption bands at 370-475 nm should be due to intramolecular ICT transitions. Both two PXZ-based analogues show strong absorption bands centered at about 340 nm and weak bands at 430 nm, which should be assigned to the  $\pi$ - $\pi$ \* transition of PXZ ring and ICT transition. Upon photoexcitation, these compounds emit strong fluorescence in dilute toluene solutions with peak wavelengths at 453, 522, 583, 578, 615, 620 nm, respectively, as illustrated in Figure 2b.The emitting color of this series of compounds continuously cover the whole visible light range from blue to red. It can be deduced that the fluorescence should originate from the ICT excited state of these molecules based on the structureless spectra profile. The results indicate that acceptor and donor groups play a leading role in the emission color of luminescent materials. Figure S2 shows the low-temperature (LT) fluorescence and phosphorescence spectra of these compounds in frozen dimethyl tetrahydrofuran (2-Me-THF) at 77 K. The energy levels of the  $S_1$ and  $T_1$  states are calculated from the peak wavelength of the highest-energy fluorescence and phosphorescent subbands. The  $S_1$ - $T_1$  energy splittings ( $\Delta E_{ST}$ ) are calculated as 0.53, 0.03, 0.09, 0.06, 0.04 and 0.02 eV for Q-Cz, Q-DMAC, *i*PP-DMAC, PP-DMAC, *i*PP-PXZ and PP-PXZ, respectively. All the pertinent data

are summarized in Table 1. It is obvious that Q-Cz possess much larger  $\Delta E_{ST}$  than all other five analogues. In contrary, the extremely low  $\Delta E_{ST}$  values imply that efficient thermally activated RISC from T<sub>1</sub> to S<sub>1</sub> and thus delayed fluorescence may be expected to occur in five DMAC and PXZ based compounds.<sup>34</sup>



**Figure 2**. UV-vis absorption and fluorescence spectra in dilute toluene solutions  $(10^{-5} \text{ mol } \text{L}^{-1})$  at room temperature.

| Compound         | $\lambda_{abs}{}^a$ | $\lambda_{em}^{a}$ | $\lambda_{em}^{b}$ | $T_{\rm d}/T_{\rm g}^{\rm c}$ | HOMO <sup>d</sup> | LUMO <sup>d</sup> | $\Delta E_{\rm ST}^{e}$ | ${\varPhi_{\mathrm{PL}}}^{\mathrm{t}}$ | $	au_{ m PF}/	au_{ m DF}$ $^{ m g}$ |
|------------------|---------------------|--------------------|--------------------|-------------------------------|-------------------|-------------------|-------------------------|--|-------------------------------------|
|                  | (nm)                | (nm)               | film(nm)           | (°C)                          | (eV)              | (eV)              | (eV)                    | film(%)                                | (ns)/(µs)                           |
| Q-Cz             | 293/341/368         | 453                | 451                | 422/NF                        | -5.61             | -2.99             | 0.53                    | 29                                     | 3.0/-                               |
| Q-DMAC           | 284/340/400         | 522                | 501                | 367/124                       | -5.27             | -2.99             | 0.03                    | 38                                     | 20.4/6.8                            |
| <i>i</i> PP-DMAC | 287/341/414         | 583                | 524                | 389/NF                        | -5.25             | -3.26             | 0.06                    | 87                                     | 19.8/69.7                           |
| PP-DMAC          | 286/345/409         | 578                | 545                | 425/137                       | -5.25             | -3.29             | 0.09                    | 83                                     | 48.2/21.2                           |
| iPP-PXZ          | 287/329/437         | 615                | 578                | 407/131                       | -5.01             | -3.26             | 0.02                    | 65                                     | 32.1/1.0                            |
| PP-PXZ           | 287/335/438         | 620                | 591                | 164/NF                        | -5.01             | -3.30             | 0.04                    | 31                                     | 48.4/0.8                            |

Table 1. Physical data summary of new compounds.

<sup>a</sup> Absorbance and PL measured in toluene solutions at room temperature, taken from Fig. 2; <sup>b</sup> PL of TADF emitters in CBP films (5 wt%), Q-Cz in mCP film (5 wt%), taken from Fig. S3f; <sup>c</sup>  $T_d$ : decompose temperature corresponding to 5% weight loss; <sup>d</sup> HOMO and LUMO levels were calculated by CV data; <sup>e</sup>  $\Delta E_{ST} = E_S - E_T$ , both  $E_S$  and  $E_T$  were determined from the fluorescence and phosphorescence spectra at 77 K; <sup>f</sup> PL quantum yield for these compounds doped in CBP (5 wt%), measured by integrating sphere; <sup>g</sup> Lifetimes of prompt fluorescence ( $\tau_{PF}$ ) and delayed fluorescence ( $\tau_{DF}$ ) for the doped films of these compounds in CBP (5 wt%) at room temperature.

Transient PL decay property. To reveal the different light-emitting property of

these compounds, the time-resolved transient decay measurements were performed for their doped films in 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) host. When these doped films were excited by a picosecond laser by means of time-correlated single photon counting (TCSPC) technique, a prompt fluorescence (PF) with the typical lifetime ( $\tau_{PF}$ ) of 3.0, 20.4, 48.2, 19.8, 48.4 and 32.1 ns were detected for each of them at room temperature, respectively, as shown in Figure 3a and Figure S3. When these films were excited by a microsecond lamp using multi-channel scanning (MCS) technique, long lifetime component was not detected for Q-Cz, indicating that Q-Cz does not possess the delayed fluorescence property. While a long-lifetime emitting component was detected for all other five compounds with the decay lifetime ( $\tau_{DF}$ ) of 6.8, 21.2, 69.7, 0.8 and 1.0 µs (Figure S3 a-e), respectively, which should be assigned as delayed fluorescence (DF) as judged from the fact the delayed components have similar emitting wavelength to the PF of each compound. Apparently the delay fluorescence lifetimes of DMAC-based compounds are all longer than those of PXZ-based compounds. To explore the generation mechanism of the delayed fluorescence observed for these five DMAC- and PXZ-based compounds, temperature-dependent transient PL decay were measured from 100 K to 300 K, and decay curves are shown in Figure 3. It can be discerned that the fluorescence lifetimes of these compounds increased with temperature, which is a typical character for TADF emitters. This indicates that high temperature is favorable for RISC and emission of delayed fluorescence. Along with the extremely small  $\Delta E_{ST}$  values (Table 1), the observed temperature-dependent feature of PL decay for these DMAC- and

PXZ-based compounds confirms that their delayed fluorescence is really generated by TADF mechanism.

The PL quantum yield ( $\Phi_{PL}$ ) of these emitters doped in CBP films (5 wt%) were measured using an integrating sphere as 29%, 38%, 87%, 83%, 65% and 31%, respectively. According to the  $\Phi_{PL}$  and lifetime values, the prompt fluorescence quantum yield ( $\Phi_{PF}$ ), delayed fluorescence quantum yield ( $\Phi_{DF}$ ), radiative decay rate constant of S<sub>1</sub> state ( $k_r^{S}$ ), the intersystem crossing (ISC) rate constant ( $k_{ISC}$ ), and the reverse ISC rate constant ( $k_{RISC}$ ) of the five TADF emitters were estimated and listed in Table S1. Among the four TADF emitter with PP and *i*PP acceptors, the DMAC-based PP-DMAC and *i*PP-DMAC showed much higher delayed fluorescence quantum yields  $\Phi_{DF}$  of 46% and 48%, in contrast to 5% and 14.3% for PXZ-based PP-PXZ and *i*PP-PXZ. At the same time, the  $\Phi_{DF}/\Phi_{PF}$  ratios of PP-DMAC and *i*PP-DMAC are also much higher than those of PP-PXZ and *i*PP-PXZ. These indicate that the DMAC donor, relative to PXZ, should be more favorable for high TADF efficiency when PP and *i*PP are used as acceptors to design TADF emitters.



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**Figure 3**. Transient PL decay curves of 5 wt% PP/*i*PP-DMAC and PP/*i*PP-PXZ doped CBP films at various temperatures.

**Theoretical calculations.** The density functional theory (DFT) calculations were performed to get insight on the different light-emitting feature of these quinoxaline and pyrido[x,y-b]pyrazine based compounds. As shown in Figure 4, all these compounds have similar wedgeshaped conformation. The central acceptor Q, PP, or *i*PP in each molecule has the almost same dihedral angles (36-38<sup>°</sup>) with the two suspended phenylenes bridges. However, the terminal donor rings, i.e. Cz, DMAC, or PXZ, have different distorsion extents with the phenylene bridges. For all analogues containing DMAC and PXZ rings, these donor rings are almost perpendicular to the phenylene bridges with large dihedral angles of 71.86 to 89.35<sup>°</sup>. It is reasonable since this highly twisted conformations can effectively avoid the steric repulsion of

hydrogen atoms of the cross-linked phenylene and DMAC and PXZ rings.<sup>35</sup> While for carbazole based Q-Cz, the carbazole ring has much smaller dihedral angle  $(50.34^{\circ})$ with the pheneylene bridges, suggesting less twisted conformation for Q-Cz relative to other five analogues. The highest occupied molecule orbital (HOMO) of Q-Cz is mainly located on terminal carbazole rings, with small contribution from the bridging phenylene rings, while the lowest unoccupied molecule orbital (LUMO) is distributed on the quinoxaline part. Apparently, the HOMO and LUMO have sufficient overlap with each other due to the less twisted conformation and result in the efficient  $\pi$ -conjugation between donor and acceptor. In contrast, the HOMOs of Q-DMAC and other DMAC- and PXZ-based analogues are exclusively located on the terminal donor rings, while their LUMOs are mainly located on the Q, PP or *i*PP acceptor rings with tiny spreading on the phenylene rings, with almost no spatial overlap between donors and acceptors owing to the highly twisted donors relative to the bridging phenylenes. The noticeable spatial overlap of HOMO/LUMO should interpret the relatively large  $\Delta E_{ST}$  (0.53 eV) of Q-Cz and normal fluorescence behavior observed in photophysical study. In contrast the highly twisted structures of all DMAC- and PXZ-based analogues prevent orbital interaction between electron-donating and withdrawing moieties, leading to the well-separated HOMOs and LUMOs. The complete spatial separation of HOMOs and LUMOs provides a weak exchange interaction between HOMOs and LUMOs and results in sufficiently small  $\Delta E_{ST}$  (0.02) -0.09 eV) to induce efficient  $S_1 \leftarrow T_1$  RISC and finally generate TADF.<sup>36</sup> It should be noted that the HOMOs of these compounds look like not eaqually distributed on two

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donor rings (Figure 4), although the two donor parts are chemically equivalent in these symmetrical molecules. In fact, as judged by the almost identical energies of HOMO and HOMO-1 orbitals (Figure S4) for these molecules,<sup>37</sup> the two terminal donor rings should have identical contribution to their HOMOs and they are energetically equivalent.



optimized structures of the investigated molecules in their S<sub>0</sub> state level.

**Electrochemical properties.** The electrochemical redox activity of these compounds were investigated by using cyclic voltammetry (CV), and the cyclic voltammograms are shown in Figure 5, and the corresponding data are summarized in Table 1. These compounds showed quasi-reversible oxidation and reversible reduction waves, indicating these materials have excellent electrochemical stability. It would be reasonable to assign the oxidation wave of each compound to the one-electron donation of the carbazole, DMAC and PXZ part, and the reduction to the electron withdrawing on quinoxaline, PP and *i*PP moieties. During the anodic scan, Q-Cz and

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Q-DMAC showed a quasi-reversible oxidation peak with the onset potential of the first oxidation wave  $(E_{ox}^{onset})$  at 1.210 V and 0.874 V. The other two DMAC-based compounds *i*PP-DMAC and PP-DMAC exhibit the  $E_{ox}^{onset}$  of 0.859 V and 0.852 V, respectively. At the same time the both PXZ-based compounds *i*PP-PXZ and PP-PXZ have same  $E_{ox}^{onset}$  of 0.609 V. It is evident that the  $E_{ox}^{onset}$  becomes lower and lower with the donor going in the order of Cz, DMAC, and PXC, indicating that these compounds can be oxidized more and more readily due to the reduced oxidation potential of the donor part. For the isomers containing same donor but different acceptors, e.g. *iPP-DMAC* and *PP-DMAC* or *iPP-PXZ* and *PP-PXZ*, the  $E_{ox}^{onset}$  are almost identical to each other. This is reasonable since the oxidaiton of these compounds occur on the donor part within these molecules. During cathodic scan, the quinoxaline based two compounds Q-Cz and Q-DMAC were electrochemically reduced at much lower potentials with the onset potential of the first reduction wave  $(E_{red}^{onset})$  at -1.408 V and -1.410 V. With the acceptor going to *i*PP and PP, the reduction occurred at much lower  $E_{red}^{onset}$  of -1.139 V, -1.113 V, -1.139 V and -1.101 V for iPP-DMAC, PP-DMAC, iPP-PXZ and PP-PXZ, respectively. For the isomers with same donor groups, e.g. iPP-DMAC and PP-DMAC, or iPP-PXZ and PP-PXZ, the isomers containing PP acceptor has less negative reduction potentials than iPP-based isomers. This further proves that PP has slightly stronger electron withdrawing ability than *i*PP, both which have stronger electron withdrawing ability than quinoxaline (Q). The HOMOs and LUMOs energy levels of these compounds were determined with the empirical equations  $E_{\text{HOMO}} = -e(E_{\text{ox}}^{onset} + 4.4)$  and  $E_{\text{LUMO}} = -e(E_{red}^{onset} + 4.4)$ .<sup>38</sup> The

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HOMO levels of these compounds were estimated to be -5.61 eV, -5.27 eV -5.25 eV, -5.25 eV, -5.01 eV and -5.01 eV, and the LUMOs are -2.99 eV, -2.99 eV, -3.26 eV, -3.29 eV, -3.26 eV and -3.30 eV, respectively. The electrochemical band gap ( $E_g$ ) of each compound was calculated as the potential difference between  $E_{ox}^{onset}$  and  $E_{red}^{onset}$ multiplied by the electron charge (*e*). The  $E_g$  are determined as 2.62, 2.28, 1.99, 1.96, 1.75, and 1.71 eV for Q-Cz, Q-DMAC, *i*PP-DMAC, PP-DMAC, *i*PP-PXZ and PP-PXZ, respectively. Evidently the regular change in electrochemical band gaps of these compounds is in consistent with and can well account for the trend observed in their fluorescence wavelength and emitting color. Therefore, by gradually increasing the electron donating ability of donor unit and simultaneously increasing the electron withdrawing ability of acceptor, the fluorescence of the constructed D- $\pi$ -A type compounds have successfully been tuned from pure blue via green and yellow to orange-red, covering the whole visible light range.



Figure 5. Cyclic voltammograms of the compounds measured in  $CH_2Cl_2/DMF$  solutions. The black dotted lines schematically indicate the onsets of oxidation and reduction for each compound.

Electroluminescence property. To evaluate the performance of these compounds as light emitters, multilayer OLED devices were fabricated. Based on the high excited state energy of the blue fluorescent Q-Cz, after a careful exploration of different device configurations, different hosts and a high-energy host 1,3-di(9H-carbazol-9-yl)benzene (mCP) was selected for it to fabricate blue OLED with the device structure of ITO/PEDOT:PSS (40 nm)/NPB (20 nm)/mCP:Q-Cz (2 wt%, 20 nm)/TPBI (30 nm)/LiF (1 nm)/Al (200 nm). In this device, poly(3, 4-ethylenedioxythiophene) (PEDOT:PSS) was used as the hole-injecting layer, N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) the as hole-transporting layer (HTL), 1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBI) as electron-transporting layer (ETL) and hole-blocking layer (HBL), LiF and Al as the electron-injecting material and the cathode, respectively. While for other five TADF emitters with emitting color from sky-blue to orange-red, a relatively low-energy host, 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP,  $E_T$ =2.6 eV) was selected to fabricate the OLEDs with configuration of ITO/PEDOT:PSS (40 mn)/TAPC (20 nm)/CBP:TADF emitter (5 wt% or 10 wt%, 20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (200 nm). In these devices, 1,1-bis[4-[N,N-di(p-tolyl)-amino] phenyl]cyclohexane (TAPC) and 1,3,5-trif(3-pyridyl)-phen-3-yl]benzene (TmPyPB) were employed as the HTL and ETL. In order to confine light-emiting excitons in the emitting layers, the adjacent layers including NPB, TPBI, TAPC and TmPyPB were selected to possess higher singlet and tripet energies than the dopant in the light-emitting layers in both types of OLEDs. The energy level diagrams and the chemical structures of the related

materials used in OLEDs are shown in Figure S5. The HOMOs and LUMOs of these TADF emitters are sandwiched between those of the CBP host, relatively equilibrium hole and electron capture abilities can be obtained.<sup>39</sup> For the blue device of Q-Cz, the doping concentration was set as 2 wt% due to its traditional fluorescence feature. While all other TADF emitters based OLEDs, the doping concentration was explored from 5 wt% to 10 wt% for performance optimization. And it was observed that 5 wt% devices exhibited much higher efficiencies than higher dopong levels. As a special case, additional concern was raised on the chemical stability of PP-PXZ and the reliability of its OLED data since a weight loss was detected at a low temperature of 164  $\,^{\circ}$ C in TGA measurement (Table 1 and Figure S1). No new product or obvious impurity was found in the residue after thermal evaporation of PP-PXZ during the device fabrication of 5 wt% device, as confirmed by the thin layer chromotagraphy (TLC) detection on the residue. And the fluorescence spectra of the evaporated PP-PXZ films and 5 wt% OLED did not show discrepancy in terms of spectral profile to its inherent PL spectra in dilute solution. These imply that the thermal deposited PP-PXZ did not encounter decomposition if slowly and carefully heated and its EL data are reliable in the case of 5 wt% OLED. However, slight thermal decomposition was observed for PP-PXZ during device fabrication of 10 wt% device, as verified by the darkening of the residue after thermal evaporation and simutaneous detection of a new strong polar impurity in the residue by TLC and a weak <sup>1</sup>H NMR signal at a chemical shift of about 6.1. Thermal decomposition was possible for PP-PXZ when it was heated and evaporated more rapidly to reach a higher doping concentration.

Actually a slightly higher heating temperature was applied on the sample to get higher doping concentration, which along with the long-time heating operation result in thermal decomposition of PP-PXZ. The EL spectra, the current density-voltage-brightness (*J-V-B*) characteristics, and the efficiency curves for the TADF OLEDs are depicted in Figure 6, and those for blue device of Q-Cz are provided in Figure S6 in supporting information. All the electroluminescence (EL) data are summarized in Table 2.

The Q-Cz based OLED exhibited pure blue electroluminescence (EL) with emission peak at 436 nm, the full width at half maximum (FWHM) of 50 nm, and Commission Internationale de l'Éclairage (CIE) color coordinates of (0.16, 0.07), as indicated by the EL spectra in Figure 6a and data in Table 2. Obviously the CIE coordinates of Q-Cz device are quite close to (0.14, 0.08) for standard blue light. This blue device turned on (to delievered a brightness of 1 cd m<sup>-2</sup>) at a voltage of 4.8 V ( $V_{on}$ ), and exhibited a maximum brightness ( $L_{max}$ ) of 1480 cd m<sup>-2</sup>, a maximum current efficiency ( $\eta_c$ ) of 0.7 cd A<sup>-1</sup>, corresponding to a peak forward viewing external quantum efficiency (EQE,  $\eta_{ext}$ ) of 1.2% and a power efficiency ( $\eta_p$ ) of 0.5 lm W<sup>-1</sup> (Figure S6).

At a doping level of 5 wt%, the five TADF OLEDs turned on at 3.1-3.5 V and exhibited bright sky-blue via green and yellow to orange-red EL, as illustrated by the EL spectra in Figure 6a. The EL of all these six OLEDs successfully cover almost the whole visible light range from pure blue to orange-red, which should benefit from the appropriate molecular designing by adjusting ICT extent through varying the donor and acceptor groups. The EL peak wavelengths of all these TADF emitters at the doping level of 5 wt% (Table 2) are identical to or slightly red-shifted relative to the PL peak wavelengths of their doped films in CBP host (Table 1 and Figure S3 f). For example, the O-DMAC device shows a EL peak at 512 nm, which is red-shfted by 11 nm relative to its PL in CBP film (501 nm), while iPP-DMAC exhibits identical EL and PL peak wavelength at 524 nm. The red shift of EL spectra in comparison with the corresponding PL should be caused by the influence of the electrical field in OLEDs on the light-emitting molecules, as frequenly observed in various types of OLEDs. These five TADF OLEDs have much lower  $V_{on}s$  (3.1-3.5 V) than the Q-Cz device (4.8 V), which may be ascribed to the enhanced hole and electron injections into the emitting layer due to both reduced electron barriers and hole barrier at the emitting layer interfaces in comparison with Q-Cz device. As shown by the energy level diagram in Figure S5, the LUMOs and HOMOs of all TADF emitters are sandwiched within those of CBP host and even the adjacent layers, which must result in direct charge traps by the dopant molecules as an important excitation way in addition to the host-dopant energy transfer. For example, in Q-DMAC based TADF device (Figure S5 b), the hole injecting barrier from TAPC to CBP host is 0.19 eV, from TAPC to Q-DMAC is -0.23 eV, while the electron injecting barrier from TmPyPB to CBP is 0.50 eV, from TmPyPB to Q-DMAC is -0.26 eV. This indicates that both hole injection and electron injection from adjacent layers direct onto Q-DMAC are sponteneous processes, which must facilitate the charge injection into emitting layer and help to reduce driving voltage of the devices. However, in Q-Cz

NPB direct to Q-Cz is 0.11 eV. While the electron injecting barrier from TPBi to mCP is 0.51 eV, and from TPBi direct to Q-Cz is -0.29 eV. Apparently in both TADF devices and O-Cz device, the hole barriers and electron barriers from adjacent layers into the host are almost comparable to each other. However, direct charge trapping by the dopant seems be much easier in TADF devices than in Q-Cz device, which should contribute to the relatively lower turn-on voltages for these TADF devices. These five TADF OLEDs all exhibited much higher EL efficiencies than the Q-Cz device, this is reasonable since the TADF nature of these dopant emitters must have extra contribution to the brightness and efficiencies of OLEDs due to highly efficient harvesting of both electrogenerated singlet and triplets excitons for light emission by TADF emitters. The Q-DMAC and iPP-DMAC based devices exhibited green emission with EL peaks at 512 and 524 nm, and maximum  $\eta_c$  of 35.9 cd A<sup>-1</sup> and  $\eta_{ext}$ of 12.9% for Q-DMAC device, and  $\eta_c$  of 51.9 cd A<sup>-1</sup> and  $\eta_{ext}$  of 16.7% for *i*PP-DMAC device. Under identical conditions, the isomer PP-DMAC based device exhibited yellow EL with peak at 563 nm and maximum efficiencies of 42.4 cd  $A^{-1}$  and 14.1%. With donor going to PXZ, two PXZ-based TADF emitters exhibited yellow and orange-red EL in their OLEDs, respectively. The iPP-PXZ based OLED exhibited yellow emission with peak at 584 nm and maximum efficiencies of 30.6 cd A<sup>-1</sup> and 12.3%. While its isomer PP-PXZ based OLED exhibited orange-red emission with peak at 594 nm and efficiencies of 30.6 cd  $A^{-1}$  and 13.0%.

device (Figure S5 a), the hole injecting barrier from NPB to mCP is 0.22 eV, from

In comparison with the quinoxaline based Q-DMAC, the other four TADF

increasing brightness, as illustrated by the efficiency curves in Figures 6c and 6d. For example, at the high brightness of 100, 1000 and 5000 cd m<sup>-2</sup>, the  $\eta_{ext}$  of Q-DMAC device are at 5.86%, 2.15% and 1.20%, which represent the efficiency roll-off by 54.6%, 83.3%, and 90.7% relative to the maximum  $\eta_{ext}$  (12.9%). In contrary, at the high brightness of 100, 1000 and 5000 cd m<sup>-2</sup>, the PP-PXZ (as an example) device still remain high  $\eta_{ext}$  at 12.98%, 11.10% and 4.63%, representing the efficiency roll-off by 0.2%, 14.6% and 64.4% relative to the maximum  $\eta_{ext}$  value (13.0%). It is supposed that the more stable efficiencies of these four iPP and PP based TADF emitters in comparison with another TADF analogue Q-DMAC should benefit from the incorporation of iPP and PP acceptors in these TADF molecules. It can also be discerned that two PP-based analogues show higher EL efficiencies under high current density region than their iPP-isomers, although the iPP-based isomers may exhibit higher or at least comparable efficiencies with the PP-based isomers at low brightness region. This implies that the PP-based analogues may possess better stability to withstand high driving current density or high brightness. Furthermore, two DMAC-based TADF emitters (iPP-DMAC and PP-DMAC) exhibited high efficiencies than their PXZ analogues (iPP-PXZ and PP-PXZ), as shown in Table 2 and Figure 6. This can be mainly attributed to the higher PLQYs of DMAC-based emitters than the PXZ-based analogues.

emitters based on iPP and PP acceptors show more stable EL efficiencies with

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![](_page_25_Figure_2.jpeg)

**Figure** 6 EL spectra (a) for all six OLEDs, and *J-V-B* characteristics (b) and the efficiency curves (c and d) for five TADF OLEDs at 5 wt% doping concentration.

| Table | 2.              | Summary     | y of | EL   | data  | tor   | all  | OLEDs     | based | on | blue | fluorescent | Q-Cz | and |
|-------|-----------------|-------------|------|------|-------|-------|------|-----------|-------|----|------|-------------|------|-----|
| TADF  | <sup>7</sup> ma | aterials at | vari | ious | dopir | ng co | once | entration | s.    |    |      |             |      |     |

| Concent. | Emitter  | V <sub>on</sub><br>(V) | $L_{\rm max}$<br>(cd m <sup>-2</sup> ) | $\eta_{\rm c}$<br>(cd A <sup>-1</sup> ) | $\eta_{\rm P}$<br>(lm W <sup>-1</sup> ) | $\eta_{\rm ext}$ (%) | λ <sub>em</sub><br>(nm) | $\operatorname{CIE}(x,y)$ |
|----------|----------|------------------------|--|---|---|----------------------|-------------------------|---------------------------|
| 2 wt%    | Q-Cz     | 4.8                    | 1480                                   | 0.7                                     | 0.5                                     | 1.2                  | 436                     | 0.16,0.07                 |
|          | Q-DMAC   | 3.5                    | 6850                                   | 35.9                                    | 32.2                                    | 12.9                 | 512                     | 0.27,0.49                 |
|          | iPP-DMAC | 3.5                    | 13900                                  | 51.9                                    | 43.5                                    | 16.7                 | 524                     | 0.32,0.56                 |
| 5 wt%    | PP-DMAC  | 3.5                    | 16500                                  | 42.4                                    | 31.3                                    | 14.1                 | 563                     | 0.44,0.53                 |
|          | iPP-PXZ  | 3.1                    | 13400                                  | 30.6                                    | 30.5                                    | 12.3                 | 584                     | 0.49,0.50                 |
|          | PP-PXZ   | 3.4                    | 19500                                  | 30.6                                    | 24.6                                    | 13.0                 | 594                     | 0.52,0.46                 |
| 10 wt%   | Q-DMAC   | 4.0                    | 4790                                   | 28.3                                    | 22.2                                    | 9.8                  | 518                     | 0.30,0.52                 |
|          | iPP-DMAC | 4.1                    | 6140                                   | 18.3                                    | 18.7                                    | 7.8                  | 550                     | 0.47,0.54                 |
|          | PP-DMAC  | 3.9                    | 4710                                   | 21.4                                    | 13.5                                    | 7.7                  | 573                     | 0.47,0.52                 |
|          | iPP-PXZ  | 3.6                    | 15000                                  | 20.0                                    | 17.2                                    | 9.6                  | 598                     | 0.54,0.46                 |
|          | PP-PXZ   | 3.4                    | 7160                                   | 20.6                                    | 19.0                                    | 9.3                  | 595                     | 0.53,0.46                 |

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The doping concentration of TADF emitters was increased to 10 wt% with same device structure as above 5 wt% devices to explore the possibility of performance optimization. The J-V-B characteristics, EL spectra, and the efficiency curves for these 10 wt% TADF OLEDs are described in Figure S7, and EL data are summarized in Table 2. In comparison with the 5 wt% OLEDs, the EL spetra of these 10 wt% devices all red shifted by 10-24 nm. At the same time, the EL efficiencies also decreased to some extent with increasing doping level. For example, the Q-DMAC device at 10 wt% exhibited a maximum  $\eta_{ext}$  of 9.8% (vs 12.9% at 5 wt%), and the *i*PP-PXZ device at 10 wt% exhibited a maximum  $\eta_{ext}$  of 9.6% (vs 12.3% at 5 wt%). The spectral red-shift along with efficiency decrease with increasing doping concentration has been frequently observed in TADF OLEDs mainly due to concentration quenching effect.<sup>40,41</sup> Similar to the observation in 5 wt% TADF OLEDs, in 10 wt% devices, the PP-DMAC device showed higher efficiencies and enhanced efficiency stability at high brightness region than isomer iPP-DMAC, and all these PP- and iPP-based TADF emitters exhibited higher efficiencies than the quinoxaline based Q-DMAC. However, the efficiencies of PP-PXZ device at 10 wt% are exceptionally reduced in comparison with its isomer iPP-PXZ, which is in contrary to the case at 5 wt% doping level. This should be because the PP-PXZ was partially decomposed when it was rapidly heated for a higher doping concentration, as proved by the detection of impurity in residue of PP-PXZ after device fabrication.

#### Conclusions

In summary, by introducing one sp<sup>2</sup>-hybridized N atom into different sites of the quinoxaline (Q) ring, the novel acceptors pyrido[2,3-b]pyrazine (PP) and pyrido[3,4-b]pyrazine (iPP) were generated with enhanced electron withdrawing abilities relative to the parent O to different extent. A series of wedge shaped compounds were designed and synthesized by attaching two electron donors (D), i.e., carbazole (Cz), 10-dimethyl-acridine (DMAC) or 10H-phenoxazine (PXZ), symmetrially on the central acceptor (A) unit such as Q, PP or *i*PP. The luminescent behavior of these compounds greatly depends on the combination style of donor and acceptor and the resultant steric configuration. By increasing the molecular distorsion angles due to enhanced steric hindrance with the donor going from Cz to DMAC, the light emission was tuned from the normal fluorescence of Q-Cz to the TADF of Q-DMAC. And all the DMAC- and PXZ-based compounds in present study have TADF feature mainly due to the inherent three six-membered ring structures of DMAC and PXZ moieties and thus the highly twisted molecular structures. It has been confirmed by electrochemical measurements and theoretical calculations that the electron donating ability stepwisely increases in the order of Cz, DMAC and PXZ, while the electron withdrawing ability increases gradually in the order of O, *iPP*, and PP. Therefore, by gradually enhancing the intramolecular charge transfer extent by combining appropriate D and A, the emission color of this series of compounds were regularly tuned from pure blue via green and yellow to orange-red. The OLEDs containing these compounds doped emitters exhibited full-color as electroluminescence covering the whole visible light range. The Q-Cz based OLEDs

exhibited an external quantum efficiency ( $\eta_{ext}$ ) of 1.2% with pure blue color coordinates of (0.16, 0.07). All other TADF-OLEDs showed green to orange-red EL with moderate to high  $\eta_{ext}$ s from 12.9% (35.9 cd A<sup>-1</sup>) to 16.7% (51.9 cd A<sup>-1</sup>). All the PP and *i*PP based TADF emitters have improved efficiency stabilities than the quinoxaline based analogues, suggesting that PP and *i*PP should be ideal acceptor units to construct novel light-emitting materials, especially those low-cost and high-performance TADF emitters for OLED applications.

#### **Experimental Section**

General Information. The <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra were characterized by a Bruker Avance III 400 and 101 MHz and Bruker Avance III 500 and 126 MHz spectrophotometer and HP1100LC/MSD MS spectrometer. A PerkinElmer Lambandda 35 spectrophotometer PerkinElmer LS55 spectrometer were used to measure UV–vis absorption, fluorescence and phosphorescence spectra, respectively. Photoluminescence quantum yields (PLQYs) of films were measured on a HAMAMATSU absolute PL quantum yield spectrometer C11347. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) were measured by using a Netzsch DSC 201 and PerkinElmer thermogravimeter (Model TGA7) instrument. Transient fluorescence decays were detected with an Edinburgh Instruments FLS1000 spectrometer. Electrochemical workstation (BAS100B, USA) was used to performe the cyclic voltammetry study. Density functional theory (DFT) calculations using B3LYP functional were performed with Gaussian 09.

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OLED fabrication and measurements. Before evaporating organic film and preparation device, the ITO glass substrates were precleaned with acetone, isopropanol detergents and deionized water successively, and treated by oxygen plasma for 30 min. The sample then was transferred into a deposition chamber. Devices were prepared by evaporating organic layers at a rate of 1.0 Å s<sup>-1</sup> onto the ITO substrate sequentially at a pressure below  $1 \times 10^{-4}$  Pa. The emitting layers of OLEDs were fabricated by thermal co-evaposition of the dopant and host materials onto the hole transporting layer. The doped films for PL measurements were prepared on the cleaned quartz substrates in the same way, and have the thickness of 50 nm. The doping concentration was carefully controlled by adjusting the different evaporation rate of the host and the dopant. The thin layer of LiF (1 nm) was thermally deposited onto organic layers to facilitate electron injection and then an Al film (200 nm) was deposited as the cathode. The current-voltage-brightness characteristics and EL spectra of OLEDs were measured using Keithley 2400 SMU, Chroma Meter 200, and PR705 photometer.

**Compound syntheses.** Important intermediates a, b, and c were synthesized according to literature methods.<sup>28-31</sup>

General procedure for synthesis of 2,3-bis(4-bromophenyl)quinoxaline (d), 2,3-bis(4-bromophenyl)pyrido[3,4-b]pyrazine (e) and 2,3-bis(4-bromophenyl)pyrido[2,3-b]pyrazine (f):A mixture of pyridine-3,4-diamine or pyridine-2,3-diamine (400 mg, 3.66 mmol) and 1,2-bis(4-bromophenyl)ethane-1,2-dione (1340 mg, 3.66 mmol) in glacial acetic acid

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(40 ml) was refluxed under 110 °C for 24 h. After cooling to room temperature, the solvent was poured into water and the precipitated solid are filtered under reduced pressure and the residue was purified by column chromatography on silica gel using 4:1 petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> as the eluent to give a light green solid (1.33 g or 1.40 g, 85%).

d: TOF-EI-MS (m/z): cal. for C<sub>20</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>2</sub> 437.9367; Found 437.9362 [M]<sup>+</sup>.

e: TOF-EI-MS (m/z): cal. for C<sub>19</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>3</sub> 438.9320; Found 438.9321 [M]<sup>+</sup>.

f: TOF-EI-MS (m/z): cal. for C<sub>19</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>3</sub> 438.9320; Found: 438.9329 [M]<sup>+</sup>.

Synthesis of 2,3-bis(4-(9H-carbazol-9-yl)phenyl)quinoxaline (Q-Cz): [Pd(PPh<sub>3</sub>)<sub>4</sub>] (32 mg, 0.023 mmol) and K<sub>3</sub>PO<sub>4</sub> (586 mg, 2.76 mmol) were added into the mixture 2,3-dichloroquinoxaline 0.92 solution of (184)mmol). (a) mg. 3-(9H-carbazol-9-yl)phenyl boronic acid (645 mg, 2.03 mmol) in toluene. The resulting mixture was stirred under nitrogen atmosphere at 100 °C for 12 h. Upon cooled to room temperature and removed the toluene solvent by evaporation under reduced pressure, the organic layer was dried over MgSO<sub>4</sub> and then concentrated by reduce pressure. The residue was purified by column chromatography on silica gel (petroleum ether:  $CH_2Cl_2 = 4:1$ ), giving the pure product Q-Cz as white solid, 630 mg, yield: 67%.

Q-Cz: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.30 (dd, J = 6.4, 3.4 Hz, 2H), 8.16 (d, J = 7.7 Hz, 4H), 7.95-7.84 (m, 6H), 7.73-7.64 (m, 4H), 7.49 (d, J = 8.2 Hz, 4H), 7.45-7.39 (m, 4H), 7.32 (dd, J = 10.9, 3.9 Hz, 4H). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 152.47, 141.38, 140.52, 138.55, 137.75, 131.52, 130.47, 129.28, 126.76, 126.13,

123.61, 120.39, 120.26, 109.65. TOF-MALDI-MS (*m*/*z*): cal. for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub> 612.2322; Found: 612.2328 [M]<sup>+</sup>.

General procedure for synthesis of 2, 3-bis (4-(9, 9-dimethylacridin-10(9H)-yl)

phenyl)quinoxaline(Q-DMAC),10,10'-(pyrido[3,4-b]pyrazine-2,3-diylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihyd(iPP-DMAC),roacridine(iPP-DMAC),10,10'-(pyrido[2,3-b]pyrazine-2,3-diylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine)(PP-DMAC),

10,10'-(pyrido[3,4-b]pyrazine-2,3-diylbis(4,1-phenylene))bis(10H-phenoxazine) (iPP-PXZ) and

10,10'-(pyrido[2,3-b]pyrazine-2,3-diylbis(4,1-phenylene))bis(10H-phenoxazine)

(*PP-PXZ*). Pd<sub>2</sub>(dba)<sub>3</sub> (44 mg, 0.046 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1200 mg, 3.68 mmol), and (t-Bu)<sub>3</sub>P HBF<sub>4</sub> (13 mg, 0.046 mmol) were added into the mixed solution of d, e or f (0.92 mmol) and 9,9-dimethyl-9,10-dihydroacridine (DMAC-H) or 10H-phenoxazine (PXZ-H) (2.04 mmol) in toluene. The resulted mixture was stirred under nitrogen atmosphere at 100 °C for 24 h. After removing reaction solvent by vacuum distillation, the residue was purified by column chromatography on silica gel (petroleum ether:ethyl acetate=25:1). Repeated recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH gave pure product.

Q-DMAC: light green silver flakes, 630 mg, yield 40%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.41-8.21 (m, 2H), 8.05-7.77 (m, 6H), 7.59-7.32 (m, 8H), 7.10-6.72 (m, 8H), 6.32 (d, J = 8.0 Hz, 4H), 1.70 (d, J = 17.3 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

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 $\delta$ : 152.93, 142.17, 141.37, 140.65, 138.64, 132.50, 131.31, 130.63, 130.29, 129.32, 126.51, 125.09, 120.82, 114.08, 36.03, 30.90. TOF-MALDI-MS (*m/z*): cal. for C<sub>50</sub>H<sub>40</sub>N<sub>4</sub> 696.3253; Found: 696.3253 [M]<sup>+</sup>.

*i*PP-DMAC: yellow solid, 466 mg, yield 42%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.73 (s, 1H), 8.94 (d, J = 5.7 Hz, 1H), 8.13 (d, J = 5.7 Hz, 1H), 7.88 (dd, J = 8.4, 2.4 Hz, 4H), 7.45 (dd, J = 9.9, 4.6 Hz, 8H), 6.98-6.81 (m, 8H), 6.33 (d, J = 7.5 Hz, 4H), 1.69 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 157.59, 154.96, 154.35, 147.47, 143.89, 142.78, 140.56, 140.53, 137.80, 137.75, 136.40, 132.47, 132.41, 131.47, 131.37, 130.49, 130.40, 126.51, 125.16, 121.61, 121.00, 120.95, 114.09, 114.04, 36.05, 30.87, 30.85. TOF-MALDI-MS (m/z): cal. for C<sub>49</sub>H<sub>39</sub>N<sub>5</sub> 697.3205; Found: 697.3189 [M]<sup>+</sup>.

PP-DMAC: yellow solid, 630 mg, yield 40%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.28 (dd, J = 4.2, 1.8 Hz, 1H), 8.66 (dd, J = 8.3, 1.8 Hz, 1H), 7.93 (dd, J = 18.8, 8.3 Hz, 4H), 7.84 (dd, J = 8.4, 4.2 Hz, 1H), 7.53-7.34 (m, 8H), 6.97-6.77 (m, 8H), 6.42-6.26 (m, 4H), 1.69 (d, J = 1.2 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.85, 154.52, 154.16, 149.81, 142.70, 142.59, 140.59, 140.56, 138.36, 138.07, 137.76, 136.50, 132.79, 132.45, 131.51, 131.16, 130.36, 130.30, 126.52, 126.49, 125.71, 125.15. 121.12, 120.87. 114.05, 36.02, 125.09. 113.99. 30.91. 30.84. TOF-MALDI-MS (m/z): cal. for C<sub>49</sub>H<sub>39</sub>N<sub>5</sub> 697.3205; Found: 697.3222 [M]<sup>+</sup>.

*i*PP-PXZ: orange-red solid, 504 mg, yield 49%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.70 (s, 1H), 8.93 (d, J = 5.9 Hz, 1H), 8.12 (d, J = 5.5 Hz, 1H), 7.82 (dd, J = 8.3, 3.5 Hz, 4H), 7.43 (d, J = 8.3 Hz, 4H), 6.76-6.68 (m, 4H), 6.65 (t, J = 7.6 Hz, 4H), 6.53 (dd, J = 11.0, 4.3 Hz, 4H), 5.95 (d, J = 7.9 Hz, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 

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157.22, 154.59, 154.37, 147.54, 143.96, 143.83, 140.84, 140.57, 138.09, 138.07, 136.36, 133.79, 133.75, 132.61, 132.55, 131.08, 123.41, 121.78, 121.74, 115.69, 115.67, 113.12. TOF-MALDI-MS (m/z): cal. for C<sub>43</sub>H<sub>27</sub>N<sub>5</sub>O<sub>2</sub>: 645.2165; Found: 645.2190 [M]<sup>+</sup>.

PP-PXZ: dark-red solid, 463 mg, yield 45%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.27 (dd, J = 4.2, 1.9 Hz, 1H), 8.62 (dd, J = 8.4, 1.9 Hz, 1H), 7.91-7.79 (m, 5H), 7.46-7.37 (m, 4H), 6.72-6.60 (m, 8H), 6.58-6.49 (m, 4H), 6.01-5.86 (m, 4H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.58, 154.58, 153.90, 149.72, 143.97, 140.51, 140.42, 138.45, 138.33, 138.05, 136.54, 133.84, 132.96, 132.61, 131.10, 130.82, 125.80, 123.44, 123.40, 121.72, 121.68, 115.66, 115.63, 113.15, 113.14. TOF-MALDI-MS (m/z): cal. for C<sub>43</sub>H<sub>27</sub>N<sub>5</sub>O<sub>2</sub>: 645.2165; Found: 645.2177 [M]<sup>+</sup>.

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#### **Supporting Information**

TGA thermograms, PL spectra, spatial distribution of HOMOs, Energy level diagram, EL spectra, *J-V-B* characteristics and Efficiency curves for some OLEDs.

#### **Conflicts of Interest**

There are no conflicts of interests to declare.

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#### **TOC graphic abstract**

**Pyrido[2,3-b]pyrazine**, pyrido[3,4-b]pyrazine and quinoxaline are utilized to develop novel light-emitting compounds. By appropriate combination of donor and acceptor, it is possible to tune the normal fluorescence into thermally activated delayed fluorescence, and tune the light emission from pure blue via green and yellow to orange-red.

![](_page_37_Figure_4.jpeg)