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New 1*H*-pyrazolo[3,4-*b*]quinoxaline derivatives as sharp green-emitting dopants for highly efficient electroluminescent devices

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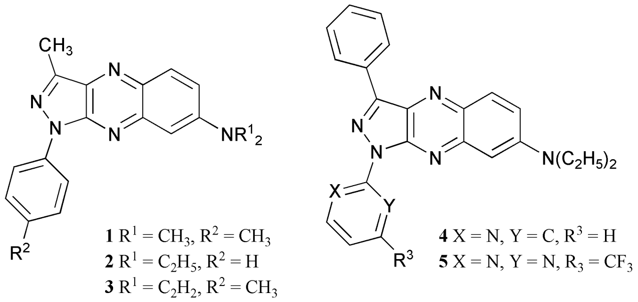
Several new 1*H*-pyrazolo[3,4-b]quinoxaline derivatives with *N*,*N*-dialkylamino as the electron donating group were prepared; their photoluminescence in solution and electroluminescence have been investigated; they show emission at about 520–540 nm with a fluorescence quantum yield close to unity in solution; devices fabricated by using these compounds as dopants show green emission with efficiencies of 7.5–9.7 cd A^{-1} and a narrow bandwidth of 65–70 nm peaking at 530–545 nm.

Organic light-emitting devices (OLEDs) have received much attention because of their potential applications in flat-panel displays.[1–4] Since the initial works on small molecule and polymer OLEDs by Tang *et al.*[5] and Friend *et al.*,[6] many research works[7,8] have focused on the improvement of efficiency and stability of OLEDs. It has been shown that doping a suitable dye into a host layer can improve both the efficiency and the stability significantly. Thus, it becomes a very important task to search for doping dyes with desired properties, such as high emission quantum yield, high thermal and photochemically stability, good colour purity *etc*. For example, doping highly fluorescent dyes, such as coumarin derivatives,[9] quinacridone and its derivatives,[10] into a host, such as tris(8-hydroxyquinolinato)aluminum (Alq$_3$) can remarkably improve the efficiency and hue of green-emitting devices. Quinoxaline derivatives are known to possess antifungal and anticancer activities. Some quinoxaline derivatives have also been explored as antidiabetic, antiallergic agents.[11] More recently, some pyrazolo[3,4-*b*]quinoxaline derivatives have been prepared and used as photoinitiators.[12] To our best knowledge, there have been no reports on the application of pyrazolo[3,4-*b*]quinoxaline derivatives in OLEDs. Herein, we report the electroluminescent and photoluminescent properties of several new pyrazolo[3,4-*b*]quinoxaline derivatives, namely 7-dimethylamino-1-(*p*-tolyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline **1**, 7-diethylamino-1-phenyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline **2**, 7-diethylamino-1-(*p*-tolyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline **3**, 7-diethylamino-1-(2-pyridyl)-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline **4**, 7-diethylamino-1-(3-trifluoromethyl-2,6-pyrimidine)-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline **5** (Fig. 1), and show that these compounds possess fluorescent quantum yields close to unity.



1 R^1 = CH$_3$, R^2 = CH$_3$
2 R^1 = C$_2$H$_5$, R^2 = H
3 R^1 = C$_2$H$_2$, R^2 = CH$_3$
4 X = N, Y = C, R^3 = H
5 X = N, Y = N, R$_3$ = CF$_3$

Fig. 1 The molecular structures of compounds **1**–**5**.

Compounds **1**–**5** were prepared with similar methods to that described in the literature[12] with modification of the purification procedure in order to get high-purity products required for OLED applications. All new compounds were purified by recrystallization, and characterized by ^{1}H NMR, MS, and elemental analysis.† The molecular structures of this series of compounds suggests that they are intramolecular charge transfer compounds with the dialkylamino moiety function as the electron donating group at the 7-position and the quinoxaline ring function as the electron acceptor. On the other hand, these compounds also belong to the fused heterocyclic aromatic ring analogues. From the viewpoint of molecular design for highly fluorescent molecules, it can be expected that such a combination of molecular structure in the same molecule will lead to the following advantages: (i) high fluorescent quantum yield due to the suppression of both the 'proximity effect'[13] from the interaction of n–π and π–π electron configuration and internal conversion decay from the free rotation of unbridged double bonds;[14] (ii) minimal self-reabsorption, especially in the solid state, due to large Stokes shifts; (iii) relatively narrow emission band resulting from the reduced vibration due to the bridged structures of the molecules.

Spectral data and fluorescence quantum yields of compounds **1**–**5** in dichloromethane are listed in Table 1. It can be seen that the absorption and emission maxima for compounds **1**–**3** with methyl groups at the 3-position are located around 445–455 nm and 525–535 nm, respectively, and show little shift for different substituents. Meanwhile, the wavelengths for the absorption and emission maxima for compounds **4** and **5** with phenyl groups at the 3-position and another electron withdrawing group at the 1-position are longer than those for compounds **1**–**3**. This result can be interpreted as the enhancement of intramolecular charge transfer and extension of the π-conjugate structure. More interestingly, all compounds show a high fluorescence quantum yield of almost unity, which is important and attractive for OLED applications.

Using compounds **1**–**5** as dopants, OLEDs with a configuration of indium–tin-oxide (ITO) coated glass/NPB (60 nm)/Alq$_3$:dopant (30 nm)/Alq$_3$ (20 nm)/Mg:Ag (200 nm) were fabricated. In the devices, *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) was used as the hole-transporting material, tris(8-hydroxyquinolinato)aluminum (Alq$_3$) was used as the host and electron-transporting material. The ITO coated glasses with a sheet resistivity of 30 Ω/☐ were

Table 1 Spectral and photophysical data of the compounds in dichloromethane (DCM) at room temperature

Compounds	1	2	3	4	5
$\lambda^{ab.}{}_{max}$/nm	446	457	456	467	468
ε/dm^3 mol^{-1} cm^{-1} × 10^{-4}	1.59	1.59	1.56	1.60	1.59
$\lambda^{em.}{}_{max}$/nm	525	536	532	538	538
$\Phi_f{}^a$	0.95	~1	~1	0.95	0.94

^{a} Fluorescent quantum yields (Φ_f) referenced to Rhodamine B in ethanol as standard, (Φ_f = 0.65).[15]

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used as the substrate and anode. The Alq_3 : dopant emission layers were prepared by co-evaporation of Alq_3 and dopants from respective cells. The cells were increasingly heated to sublimation, respectively. The thickness of layers and the dopant concentrations were monitored by an oscillating quartz monitor crystal. The light-emitting layer consists of Alq_3 and 0.7% (wt%) of the dopant. The devices with this ratio show the best performance. The electroluminescent (EL) spectra and luminance–current density–voltage characteristics of the devices were measured by using a SpectraScan PR650 spectrophotometer and a computer-controlled voltage–current source, Keithley 236, at ambient conditions. The devices doped with the compounds **1**–**5** show a bright green emission with high efficiency and a narrow emission band of 65–70 nm, which is about 65% of that from Alq_3 (about 105 nm). As an example, the efficiency–luminance–voltage characteristics of the device using compound **2** as an emitting material are shown in Fig. 2. The maximum efficiency of this device is 9.7 cd A^{-1}. In addition, it is worth noting that the luminance reaches more than 20 000 cd m^{-2} at 14 V, which is the maximum limit of our instrument. More detailed EL performances for compounds **1**–**5** are summarised in Table 2. All devices exhibit good performance with high brightness, a narrow emission band, and good efficiencies of 7.5–9.7 cd A^{-1}.

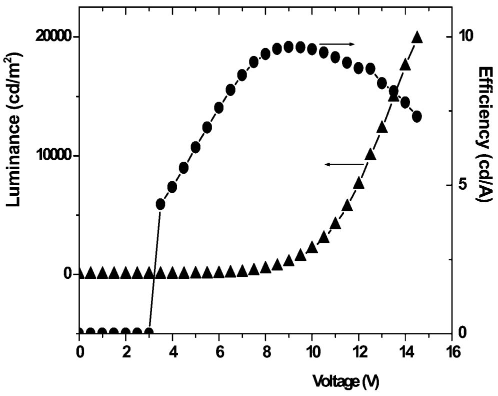

Fig. 2 Efficiency–luminance–voltage characteristics of the device with the structure NPB (60 nm)/Alq_3 : **2** (25 nm)/Alq_3 (30 nm), doping concentration: 0.7% (wt%).

Table 2 EL performances of compound-doped devices with the structure NPB (60 nm)/Alq_3 : dopant (25 nm)/Alq_3 (30 nm)[a]

		Device performance at 20 mA cm^{-2}		
Compounds	$\eta^{\max.}$	L/cd/m^2	η/cd A^{-1}	(λ (nm)
1	7.6	1600	7.6	540
2	9.7	2010	9.6	540
3	7.5	1460	7.2	536
4	9.0	1815	9.0	544
5	7.9	1400	7.1	552

[a] Doping concentration: 0.7%(wt%).

In conclusion, we have synthesized a series of new pyrazolo[3,4-*b*]quinoxaline derivatives with intramolecular charge transfer properties, and also presented the first report on the photophysical and electroluminescent behaviours of these compounds. All compounds show an extremely high fluorescence quantum yield close to unity in solution at room temperature. Green-emitting EL devices fabricated using these compounds as dopants possess very high luminance, narrow emission band, as well as good efficiency, which are comparable to the state-of-the-art high-efficiency green-emitting devices based on fluorescent dyes reported by Chen and Tang recently.[9] In addition, these compounds are easy to prepare and purify in good yields, and thus are particularly economically attractive for applications in organic EL devices. The present results suggest that the ICT compounds with structures of fused heterocyclic aromatic ring have good potential for OLED applications and warrant further exploration. We expect that the EL performance can be further improved by optimizing the device structure. Moreover, these strongly fluorescent compounds may find applications in other opto-electronic devices (*e.g.* laser dyes).

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Notes and references

† 7-Dimethylamino-1-(*p*-tolyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**1**): ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 2.44 (s, 3H), 2.83 s, 3H), 7.09 (d, J = 2.7 Hz, 1H), 7.26–7.28 (m, 1H), 7.35–7.38 (m, 1H), 7.41–7.45 (m, 1H), 8.03–8.07 (m, 1H), 8.24–8.27 (m, 2H); Anal. Calcd. For $C_{19}H_{19}N_5$: C, 71.90; H, 6.03; N, 22.07%. Found: C, 71.94; H, 6.06; N, 21.99%; MS: *m*/*z* 317 (M^+). 7-Diethylamino-1-phenyl-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**2**): ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 1.29–1.35 (m, 6H), 2.83 (s, 3H), 3.56–3.62 (m, 4H), 7.06 (d, J = 2.7 Hz, 1H), 7.26–7.30 (m, 1H), 7.35–7.40 (m, 1H), 7.52–7.58 (m, 2H), 8.00–8.05 (m, 1H), 8.42 (d, J = 8.1 Hz, 2H); Anal. Calcd. For $C_{20}H_{21}N_5$: C, 72.48; H, 6.39; N, 21.13%. Found: C, 72.56; H, 6.20; N, 20.92%; MS: *m*/*z* 331 (M^+). 7-diethylamino-1-(*p*-tolyl)-3-methyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**3**): ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 1.30-1.35 (m, 6H), 2.43 (s, 3H), 2.82 (s, 3H), 3.57–3.59 (m, 4H), 7.05 (d, J = 2.7 Hz, 1H), 7.25–7.38 (m, 3H), 8.01–8.04 (m, 1H), 8.23–8.25 (m, 2H); Anal. Calcd. For $C_{21}H_{23}N_5$: C, 73.02; H, 6.71; N, 20.27%. Found: C, 73.10; H, 6.61; N, 19.99%; MS: *m*/*z* 345 (M^+). 7-Diethylamino-1-(2-pyridyl)-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**4**): ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 1.24-1.38 (m, 6H), 3.57-3.76 (m, 4H), 7.15 (d, J = 2.7 Hz, 1H), 7.25–.29 (m, 1H), 7.41–7.61 (m, 5H), 7.93–7.99 (m, 1H), 8.10–8.12 (m, 1H), 8.55–8.58 (m, 1H), 8.74–8.78 (m, 2H); Anal. Calcd. For $C_{24}H_{22}N_6$: C, 73.07; H, 5.62; N, 21.30%. Found: C, 72.87; H, 5.84; N, 20.92%; MS: *m*/*z* 394 (M^+). 7-Diethylamino-1-(3-trifluoromethyl-2,6-pyrimidine)-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (**5**): ^1H MR (300 MHz, $CDCl_3$) δ [ppm]: 1.30–1.37 (m, 6H), 3.57–3.65 (m, 4H), 7.16 (d, J = 2.7 Hz, 1H), 7.25–7.28 (m, 1H), 7.44–7.63 (m, 4H), 8.09–8.14 (m, 1H), 8.78–8.80 (m, 2H), 9.22–9.36 (m, 1H); Anal. Calcd. For $C_{24}H_{20}F_3N_7$: C, 62.20; H, 4.35; N, 21.16%. Found: C, 62.24; H, 4.30; N, 20.83%; MS: *m*/*z* 463 (M^+).

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