Red-emitting materials derived from 2,3-dicyanopyrazine for organic light emitting devices Chun Keun Jang, Cheol Jun Song, Ji Hyun Park, Wang Yao and Jae Yun Jaung*

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Styryl-substituted derivatives of 2,3-dicyanopyrazine were designed and synthesised by the Knoevenagel condensation of 2,3-dicyano-5-methylpyrazines with 4-(diphenylamino)benzaldehyde for use as red-emitting fluorescent dyes in organic light-emitting devices. Structural analysis of the red-emitting styryl fluorescent dyes was carried out using ¹H NMR, FT-IR, and elemental analysis. The electroluminescent performance of multi-layered organic light-emitting devices fabricated with the triphenylamine-substituted dicyanopyrazine compound as the emitting layer achieved a current efficiency of 1.57 cd A⁻¹ in the green region with CIE coordinates of (0.37, 0.51). However, the green emission (525 nm) observed from the tris-(8-hydroxyquinolinato)aluminum(III) (Alq₃) electron-transport layer indicated the action of a recombination phenomenon between the emitting layer and the Alq₃ electron-transport layer. The device fabricated with the *tert*-butylphenyl-substituted compound achieved a current efficiency of 0.238 cd A⁻¹ in the red region with CIE coordinates of (0.54, 0.42) and showed no recombination phenomenon.

Keywords: 2,3-dicyanopyrazine, triphenylamine, organic light-emitting devices, Knoevenagel reaction, computational chemistry, quantum yield, red emitting material

Organic light-emitting devices (OLEDs) have potential applications in many fields including the manufacture of flat-panel displays.¹⁻⁵ Since the initial development of high efficiency OLEDs,⁶⁻⁷ much research has been focused on the development of full-colour displays with high efficiency and stability. Efficient red–green–blue emitters with good colour purity are essential for full-colour applications. Extensive study over the past decade has promoted the commercialisation of OLED devices having these required characteristics; nevertheless, further advancements are necessary for improved device performance.

In addition to efforts to modify the device structure, another effective approach to advancing OLED technology is to identify new and suitable materials for use either as host emitters or dopants. This has led to a search for materials with the desired properties such as high emission quantum yield, high thermal and photochemical stability, and good colour purity. A number of strongly emissive dyes have emerged as dopants or host emitters. Light-emitting materials for host emitters must meet the requirement for high emission quantum yield in the solid film state and must have the ability to form a thin, uniform film. They should also have suitable lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) electronic levels for electron-hole recombination confinement within the desired region to produce excitons. Besides the well-known host-emitter tris-(8-hydroxyquinolina to)aluminum(III) (Alq₃), other emitting materials have also been used as the non-doping emitting layer of OLEDs to achieve emission in additional wavelength regions and give blue, yellow, and orange colours, thus meeting the requirements of various applications. These materials include triarylamine derivatives,⁸ condensed aromatic compounds,⁹⁻¹¹ and compounds with donor-acceptor molecular structures.12-14 Furthermore, compounds with intramolecular charge transfer properties are also attractive because the incorporation of the donor and acceptor in the same molecule can lead to confinement in the recombination zone^{15,16} and hence lead to good emission.17-20

2,3-Dicyanopyrazine derivatives have become a subject of investigation because of their potentially wide applicability in colouring matters and nonlinear optical and electroluminescent (EL) materials.^{21–22} Our prior research on dyes derived from 2,3-dicyanopyrazine indicated that styryl-substituted dicyanopyrazine has a rather small molecular size but possesses a strong donor–acceptor chromophoric system. These materials exhibit strong fluorescence in both the solution and solid state, and the HOMO and LUMO electronic levels of the chromophore have been determined to be appropriate for the application of this emission layer in commonly used OLED devices.^{23–25} We now report the synthesis of dicyanopyrazine oriented styryl fluorescent dyes and evaluate their optical properties with respect to the substitution effect. The photophysical behaviour and the EL of these new derivatives are presented here.

Results and discussion

1-(4-(Diphenylamino)phenyl)propan-1-one 1a and 1-(4-tertbutylphenyl)propan-1-one 1b were synthesised using the method described previously.²⁶ The propanophenone derivative 1 was treated with bromine in CCl₄ at room temperature to produce the α -bromopropanophenone derivative **2** in 70–94% yield. The reaction of α -bromo ketones with an excess of anhydrous potassium acetate (3.5 equiv.) in acetone afforded α -acetoxy ketones, ^{27–28} and these compounds were reacted with 10% methanolic NaOH under reflux to produce the corresponding 1-aryl-2-hydroxypropan-1-one 3. The α -diketones 4 were obtained through the oxidation of α -hydroxyketones 3 with copper(II) sulfate in aqueous pyridine solution. 2,3-Dicyanopyrazines 5 were synthesised from the condensation of α diketones 4 and diaminomaleonitrile (DAMN) in the presence of a catalytic amount of *p*-toluenesulfonic acid in methanol. The methyl protons in compounds 5a and 5b were strongly deshielded and observed at 2.86 and 2.85 ppm respectively. The strong electron withdrawing effect of the cyano groups on the pyrazine ring activated the methyl group of compounds 5a and 5b, facilitating the condensation reaction with aryl aldehydes. The styryl-substituted 2,3-dicyanopyrazines 6a and 6b were synthesised by Knoevenagel condensation of the 5methyl group in **5a** and **5b** with 4-(diphenylamino)benzaldehy de in the presence of piperidine as a catalyst which followed the synthetic procedure for similar styryl dicyanopyrazines as described in the literature.²⁹ The synthetic strategy employed herein is summarised in Scheme 1.

The new compounds were characterised by FT-IR, ¹H NMR spectroscopy, and elemental analysis. Absorption bands were observed at 2227–2237 and 1604–1621 cm⁻¹ in the FT-IR spectra of compounds **6a** and **6b**, and were attributed to stretching vibrations of the CN and C=C groups, respectively. The ¹H NMR spectra of **6a** and **6b** showed doublet signals at

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Scheme 1 Synthetic route for preparation of 2,3-dicyanopyrazine derivatives.

ca 8.1–8.2 ppm indicating the presence of a typical *trans* (J = 15.6 Hz) configuration for the alkene proton at the β position from the pyrazine ring.

The optical and electrochemical data of compounds **6a** and **6b** are presented in Table 1. Compounds **6a** and **6b** showed maximum absorption wavelengths (λ_{max}) of 512 nm and 510 nm, and emission wavelengths (F_{max}) of 603 nm and 599 nm, respectively (Fig. 1). λ_{max} and F_{max} of compound **6a** were



Fig. 1 Absorption and fluorescence spectra of 6a and 6b in chloroform.

expected to be bathochromically shifted relative to those of **6b** because the triphenylamine substituent of **6a** possesses a greater electron-donating ability than the *t*-butyl phenyl group of **6b**; this is expected induce an increase in the electronic density of the former HOMO level. However, λ_{max} and F_{max} of **6a** were only slightly red-shifted, which indicates that the substituent exerts minimum effect on the electronic level of the chromophore.

Geometric optimisation of the designed structure using computational calculations was applied to explain the minimal effect of the substituent. Accelrys Materials Studio 4.3 was used for molecular design and the calculation employed the Forcite tool (molecular mechanics) and VAMP (semi-empirical method) with PM3 Hamiltonian methods. As shown in Fig. 2, the optimized structure of **6a** shows a high degree of distortion between the pyrazine ring and the bulky triphenylamine substituent. The 5-styryl substituent is distorted by 16.576°, whereas the 6-triphenylamine substituent is distorted by 53.326° relative to the 2,3-dicyanopyrazine ring. Hence, the π -conjugation between the pyrazine ring and 6-triphenylamine substituent may be more disturbed by torsional strain. In addition, the styryl substituent in the 5-position of the pyrazine ring can undergo free rotation around the $C_{5(pyrazine)}-C_{\alpha(double-bond)}$ bond; therefore, the electron-donating effect of the 5-substituent is not adversely affected by steric hindrance, thus inducing an increase in the electronic density in the HOMO level.30 The



Fig. 2 Geometrically optimised structure of **6a** (calculated with Materials Studio-Forcite MM and VAMP PM3 methods, Top view (left) and torsional angle of substituents with 2,3-dicyanopyrazine plane (right)).

increased electronic density results in compounds **6a** and **6b** exhibiting a bathochromic shift compared to compounds **5a** and **5b**.

Cyclic voltammograms (CV) were acquired in order to identify the energies of the HOMO levels of the synthesised materials. The HOMO level was calculated by assessing the oxidation potential at the first scan versus the ferrocene reference electrode. The CV results appeared stable even after 50 scanning cycles. The LUMO level was estimated from the band-gap, which was confirmed by comparison with the onset point of the UV-absorption band and from the HOMO values measured using CV (Table 1). The HOMO levels of both compounds were higher than that of N,N-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) (-5.5 eV), a known hole-transporting material. In addition, the LUMO levels were higher than that of the known electron-transporting material Alq₃ (-3.1 eV), which demonstrated that the electronic levels were adequate for use as an emitting layer. The HOMO level of **6a** was a little higher than that of **6b**, whereas the LUMO levels of both **6a** and **6b** were similar.

A multi-layered OLED device was fabricated to identify the electroluminescence (EL) properties of the synthesised materials. EL devices were fabricated using 4,4',4''-tris(*N*-3-methylphenyl-*N*-phenylamino)triphenylamine (*m*-MTDATA) as the hole-injection layer, NPB as the hole-transporting layer, Alq₃ as the electron-transporting layer, and the synthesised materials as the emitting layer. ITO and LiF/Al were used as the anode and cathode, respectively, with the following arrangement: ITO/m-MTDATA (80 nm)/NPB (15 nm)/**6a** or **6b** (30 nm)/Alq₃ (25 nm)/LiF (1.0 nm)/Al (200 nm). Fig. 3 shows the I-V curves of the devices. The device fabricated using **6a** exhibited an I–V characteristic with a slightly increased turn-on voltage.

Figure 4 shows the electroluminescence (EL) spectra of the fabricated devices. The device containing **6b** as the emitting layer emitted in the red region with a single maximum at

Table 1Optical and electrochemical properties of compounds6a and 6b

	λ_{max}/nm^a	F _{max} /nm		$\Phi_{\rm F(MEK)}{}^{\rm b}$	LUMO	номо	Eg/eV
		CHCl_3	Film		/ev	/ev	
6a	512	603	690	0.53	-2.98	-5.16	2.18
6b	510	599	685	0.13	-3.02	-5.18	2.16

^a In chloroform.

 $^{\rm b}$ Measured by comparative method in methyl ethyl ketone versus rhodamine B ($\Phi_{\rm F}$ = 0.67) in ethanol.



Fig. 3 Current density-voltage characteristics of ITO/m-MTDATA (80 nm)/NPB (15 nm)/6a(\circ) or 6b(Δ) (30 nm)/Alq3 (25 nm)/LiF (1.0 nm)/Al (200 nm) devices.



Fig. 4 EL spectrum of ITO/*m*-MTDATA (80 nm)/NPB (15 nm)/ 6a(\circ) or 6b (Δ) (30 nm)/Alq3 (25 nm)/LiF (1.0 nm)/Al (200 nm) devices at 1.0 mA cm⁻².

649 nm, whereas the device containing **6a** showed two maxima at 525 and 668 nm. The EL_{max} value at 525 nm corresponds to Alq₃ emission. The two peaks observed in the EL spectrum of the **6a** device may have resulted from the recombination zone shift to the EML/Alq₃ interface.

The HOMO levels of **6a** and **6b** were similar, as shown in Table 1, and were indicative of a low barrier similar to the HOMO level of Alq₃ (-5.7 eV), which is well-known as a green fluorescent material for OLEDs.³¹ Hence, 6a and 6b should also be suitable to act as the hole-transporting layer in such fabricated devices. However, emission from the Alq₃ layer was only observed in 6a, which indicates that 6a, containing triphenylamine substituent with greater electron-donating capacity, was simultaneously acting as a hole-transporting layer and an emitting layer. Table 2 lists the efficiency of the fabricated devices at a current density of 1.0 mA cm⁻². The device containing compound **6a** had a green CIE coordinates of (0.37, 0.51) in the green region and a current efficiency of 1.57 cd A⁻¹, whereas that containing **6b** had CIE coordinates of (0.54, 0.42) in the red region and a current efficiency of 0.238 cd A⁻¹.

Conclusions

2,3-Dicyanopyrazine derivatives synthesised in this study exhibited emission properties suitable for application in OLED devices. The electronic levels of the compounds were appropriate for such applications, falling between those of conventionally used hole- and electron-transporting layers. Compound **6a**, containing the triphenylamine substituent with greater electron-donating capacity, acted as a hole-transporting material in fabricated OLED devices, even though the HOMO level of this compound was largely similar to that of the tertbutylphenyl-substituted counterpart 6b, which did not exhibit this capacity. Transfer of excitons from Alq₃ to the electrontransport layer of other materials that have a much lower HOMO level increases the block barrier with the HOMO level of the synthesised products. This represents a method for enhancing device efficiency and verifies the suitability of 2,3-dicyanopyrazines for OLED applications.

Table 2EL performance of multi-layered devices with ITO/m-MTDATA (80 nm)/NPB (15 nm)/6a or 6b (30 nm)/Alq3 (25 nm)/LiF (1.0 nm)/Al (200 nm) arrangement at 1.0 mA cm⁻²

	EL _{max} /nm	Voltage/V	Efficiency/cd A ⁻¹	CIE (x,y)
6a	525, 668	5	1.57	(0.37, 0.51)
6b	649	5	0.238	(0.54, 0.42)

Experimental

General information

Flash chromatography was performed using Merck-EM type 60 (230– 400 mesh) silica gel (flash). Melting points are obtained using a capillary melting point apparatus and are uncorrected. Elemental analysis was performed using a Flash EA-1112 analyser. ¹H NMR spectra were recorded on a VARIAN UnityInova 300 MHz FT NMR spectrometer. UV-Vis and fluorescence spectra were measured using SCINCO S-4100 and Shimadzu RF-5301PC spectrophotometers.

The fluorescence quantum yield (Φ) was determined by a comparative method using Rhodamine B ($\Phi_f = 0.69$ in ethanol) as a reference and using the following net equation.³²

$$\Phi_{\!_{A}} = \Phi_{\!_{ref}}\!\left(\frac{PL_{\!_{A}}}{UV_{\!_{A}}}\right)\!\!\left(\frac{UV_{\!_{ref}}}{PL_{\!_{ref}}}\right)\!\!\left(\frac{n_{\!_{A}}^{\ 2}}{n_{\!_{ref}}^{\ 2}}\right)$$

where PL is the integrated area under the corrected emission spectrum and UV is the absorbance of the solution at the given excitation wavelength. Subscripts "A" and "ref" refer to the unknown and reference solutions respectively, and "n" is the refractive index of the corresponding solutions. Cyclic voltammetry (CV) experiments were performed using a BAS-100 electrochemical analyser with a threeelectrode configuration consisting of a Pt disk working electrode, an Ag/AgCl reference electrode, and Pt wire counter electrode. All measurements were taken in acetonitrile with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) as the supporting electrolyte. HOMO energy levels were calculated from the oxidation potential using the following equation.^{33,34}

HOMO (eV) =
$$-4.8 - [E_{onset} - E_{1/2}(\text{ferrocene})]$$

where E_{onset} is the onset oxidation potential (V) and $E_{1/2}$ (ferrocene) is the half-wave potential (V) of ferrocene in the solution. The electronic level of the analytes was calculated from the difference between the onset redox potential and the half-wave potential of ferrocene.

Synthesis of 1-aryl-2-bromopropan-1-ones (2); general procedure

One equivalent of Br_2 was added dropwise to a solution of the appropriate 4-substituted propanophenone **1** (0.04 mol) in CCl₄ (30 mL) with stirring at 10°C. After subsequent stirring for 2 h at room temperature, the mixture was diluted with ice water and extracted with CHCl₃ (100 mL). The organic layer was washed with water and dried with anhydrous sodium sulfate. The mixture was concentrated under reduced pressure to form the compounds **2a** and **2b**.

2-Bromo-1-[4-(diphenylamino)phenyl]propan-1-one (**2a**): Yellow solid (70%), m.p. 64 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.89 (m, ArH, 4H), 7.44–7.41 (m, ArH, 5H), 7.01 (m, ArH, 5H), 5.23 (q, *J* = 6.6 Hz, Br–C–H, 1H), 1.88 (d, *J* = 6.3 Hz, –CH₃, 3H). Anal. Calcd for C₂₁H₁₈BrNO: C, 66.33; H, 4.77; N, 3.68. Found: C, 66.12; H, 4.82; N, 3.70%; GC-MS (*m/z*) 379.75. Calcd 380.28.

2-Bromo-1-(4-tert-butylphenyl)propan-1-one (**2b**): Yellow liquid (94%); ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, J = 8.7 Hz, ArH, 2H), 7.48 (d, J = 8.7 Hz, ArH, 2H), 5.20 (q, J = 6.3 Hz, Br–C–H, 1H), 2.11 (d, J = 6.8 Hz, –CH₃, 3H), 1.40 (s, *t*-Bu, 9H). Anal. Calcd for C₁₃H₁₇BrO: C, 58.01; H, 6.37. Found: C, 58.19; H, 6.41%; GC-MS (*m/z*) 269.04. Calcd 269.18.

Synthesis of 1-aryl-2-hydroxypropan-1-ones (3); general procedure

Brominated precursor 2 (0.047 mol) and potassium acetate (0.166 mol) were heated under reflux in acetone (100 mL). The solution was filtered and the solvent was removed *in vacuo*. The intermediate α -acetoxy ketone was hydrolysed using 10% methanolic NaOH solution (100 mL) under reflux for 1 h. The mixture was diluted with water (200 mL) and then extracted with ethyl acetate (100 mL). The organic layer was washed with water, dried with sodium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography over silica gel with ethyl acetate:*n*-hexane (1:3) as the eluent, to yield the compounds **3a** and **3b**.

1-[4-(Diphenylamino)phenyl]-2-hydroxypropan-1-one (**3a**): Yellow solid (45.9%), m.p. 79 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.88 (m, ArH, 3H), 7.46 (m, ArH, 4H), 7.42 (d, ArH, 2H, *J* = 8.7 Hz), 7.16 (d, ArH, 2H, *J* = 8.7 Hz), 7.03 (m, ArH, 3H), 5.05 (q, *J* = 6.6Hz, 1H), 4.14 (s, -OH, 1H), 1.46 (d, *J* = 6.3 Hz, -CH₃, 3H); Anal. Calcd for C₂₁H₁₉NO₂: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.10; H, 6.26; N, 4.53%; GC-MS (*m/z*) 317.11. Calcd 317.38.

*1-(4-*Tert-*butylphenyl)-2-hydroxypropan-1-one* (**3b**): Yellow liquid (86%); ¹H NMR (300 MHz, CDCl₃) δ 7.86 (d, *J* = 9.0 Hz, ArH, 2H), 7.51 (d, *J* = 8.7 Hz, ArH, 2H), 5.16 (q, *J* = 6.6 Hz, 1H), 3.81 (s, –OH, 1H), 1.41 (d, *J* = 6.8Hz, –CH₃, 3H), 1.35 (s, *-t*-Bu, 9H); Anal. Calcd for C₁₃H₁₈O₂: C, 75.69; H, 8.80. Found: C, 75.36; H, 9.01%; GC-MS (*m/z*) 206.19. Calcd 206.28.

Synthesis of 1-aryl-propan-1,2-diones (4); general procedure

Compound **3** (0.018 mol) was added to a mixture of $CuSO_4$ ·5H₂O (10.16 g, 0.038 mol) in pyridine (7 mL) and water (3 mL). The mixture was heated under reflux and monitored using thin-layer chromatography [TLC, ethyl acetate:*n*-hexane (1:3)] and then extracted with ethyl acetate (100 mL) and water (150 mL). The organic layer was dried with sodium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography over silica gel with ethyl acetate:*n*-hexane (1:3) as the eluent, to yield compounds **4a** and **4b**.

1-[4-(Diphenylamino)phenyl]propan-1,2-dione (**4a**): Orange solid, (88%), m.p. 126 °C; 'H NMR (300 MHz, CDCl₃) δ 7.88 (m, ArH, 3H), 7.42 (m, ArH, 4H), 7.25 (d, *J* = 8.7 Hz, ArH, 2H), 7.15 (d, *J* = 8.7 Hz, ArH, 2H), 6.99 (m, ArH, 3H), 2.15 (s, -CH₃, 3H); Anal. Calcd for C₂₁H₁₇NO₂; C, 79.98; H, 5.43; N, 4.44. Found: C, 79.64; H, 5.49; N:4.28%; GC-MS (*m*/z) 315.04. Calcd 315.37.

1-(4-tert-Butylphenyl)propan-1,2-dione (**4b**): Yellow liquid, (75%); ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 9.0 Hz, ArH, 2H), 7.51 (d, *J* = 8.7 Hz, ArH, 2H), 2.13 (s, -CH₃, 3H), 1.34 (s, *t*-Bu, 9H); Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.64; H, 8.09%; GC-MS (*m/z*) 204.04. Calcd 204.26.

5-[4-(Diphenylamino)phenyl]-6-methylpyrazine-2,3-dicarbonitrile (**5a**): A solution of 1-[4-(diphenylamino)phenyl]propane-1,2-dione (5.0 g, 0.016 mol), diaminomaleonitrile (DAMN) (1.73 g, 0.016 mol) in methanol (200 mL) and a small amount of *p*-toluenesulfonic acid as the catalyst was heated under reflux for 2 h. Methanol was poured into the mixture and stirred for 1 h at room temperature. The precipitate was filtered off and washed with methanol. The crude product was purified by column chromatography over silica gel with ethyl acetate: *n*-hexane (1:5) as the eluent to yield compound **5a** as a yellow solid, (45%), m.p. 103 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 8.7 Hz, ArH, 2H), 7.46 (d, *J* = 8.7 Hz, ArH, 2H), 7.15–7.26 (m, ArH, 10H), 2.86 (s, -CH₃, 3H); Anal. Calcd for C₂₅H₁₇N₅; C, 77.50; H, 4.42; N, 18.08. Found: C: 77.41; H: 4.38; N: 18.16%; GC-MS (*m/z*) 386.96 Calcd 387.44.

5-(4-tert-*Butylphenyl*)-6-methylpyrazine-2,3-dicarbonitrile (**5b**): A solution of 1-(4-tert-butylphenyl)propane-1,2-dione (40 g, 0.14 mol), DAMN (15.2 g, 0.14 mol) in methanol (200 mL) and a small amount of *p*-toluenesulfonic acid as the catalyst was heated under reflux for 2 h. Methanol was poured into the mixture and stirred for 1 h at room temperature. The precipitate was filtered off and washed with methanol. The crude product was purified by column chromatography over silica gel with ethyl acetate:*n*-hexane (1:3) as the eluent, to yield compound **5b** as a white solid, (50%), m.p. 111 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 8.7 Hz, ArH, 2H), 7.54 (d, *J* = 8.7 Hz, ArH, 2H) 2.85 (s, -CH₃, 3H), 1.39 (s, *t*-Bu, 9H); Anal. Calcd for C₁₇H₁₆N₄: C, 73.89; H, 5.84; N, 20.27. Found: C, 73.74; H, 5.99; N, 19.91%; GC-MS (*m/z*) 276.15. Calcd 276.34.

(E)-5-[4-(Diphenylamino)phenyl]-6-[4-(diphenylamino)styryl]pyr azine-2,3-dicarbonitrile (6a): A solution of 5a (3.0 g, 7.74 mmol), 4-(diphenylamino)benzaldehyde (2.12 g, 7.74 mmol) in benzene (20 mL) and a small amount of piperidine as the catalyst was heated under reflux for 21 h under an N2 atmosphere. After the reaction was complete, the mixture was cooled to room temperature. Methanol was poured into the mixture and stirred for 1 h at room temperature. The precipitate was filtered off and washed with methanol. The crude product was purified by column chromatography over silica gel with ethyl acetate:n-hexane (1:3) as the eluent, to yield compound 6a as a red solid, (45%); m.p. 150 °C, FT-IR (KBr pellet), v_{max} /cm⁻¹ 2232 (C≡N), 1602 (C=C), 1489, 1296; ¹H NMR (300 MHz, CDCl₃) δ 7.82 (m, ArH, 4H), 7.78 (d, J = 15.6 Hz, 1H), 7.42 (m, ArH, 8H), 7.32 (m, ArH, 8H), 7.18 (d, J = 15.6 Hz, 1H), 7.15 (d, J = 8.7 Hz, ArH, 4H), 6.97 (m, ArH, 4H); Anal. Calcd for C₃₆H₂₉N₅: C, 82.22; H, 4.70, N, 13.08. Found: C, 81.25; H, 5.61; N. 13.37%; FAB-MS (m/z) 642.12. Calcd 642.75.

(E)-5-(4-tert-Butylphenyl)-6-[4-(diphenylamino)styryl]pyrazine-2,3-dicarbonitrile (**6b**): A solution of compound **5b** (5.0 g, 0.018 mol), 4-(diphenylamino)benzaldehyde (4.95 g, 0.018 mol) in benzene (20 mL) and a small amount of piperidine as the catalyst was heated under reflux for 21 h under an N₂ atmosphere. After the reaction was complete, the mixture was cooled to room temperature. Methanol was poured into the mixture and stirred for 1 h at room temperature. The precipitate was filtered off and washed with methanol. The crude product was purified by column chromatography over silica gel with ethyl acetate:*n*-hexane (1:3) as the eluent, to yield compound **6b** as a red solid, 45%); m.p. 143 °C; FT-IR (KBr pellet), v_{max}/cm^{-1} 2229 (C=N), 1585 (C=C), 1484, 1276; ¹H NMR (CDCl₃), δ 8.12 (d, *J* = 15.6 Hz, 1H), 7.65 (d, *J* = 8.7 Hz ArH, 2H), 7.58 (d, *J* = 8.7 Hz, ArH, 2H), 7.4 (d, *J* = 8.7 Hz, ArH, 2H), 7.12 (d, *J* = 8.7 Hz, ArH, 2H), 7.15 (m, ArH, 4H), 7.12 (d, *J* = 8.7 Hz, ArH, 2H), 7.0 (d, *J* = 8.7 Hz, ArH, 2H), 1.39 (s, *t*-Bu, 9H); Anal. Calcd for C₄₄H₃₀N₆: C, 81.33; H, 5.50, N, 13.17. Found: C, 81.71; H, 5.35; N. 13.10%; FAB-MS (*m*/z) 530.89. Calcd 531.65.

Fabrication and testing of OLED devices

OLED devices were fabricated using 4,4',4''-tris(N-3-methylphenyl-N-phenylamino)-triphenylamine (m-MTDATA), with a similar HOMO level to indium tin oxide (ITO), as the hole-injection layer. N,N-Bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) was used as the hole-transport layer. Synthesised materials **6a** and **6b** were used as the emitting layer and Alq₃ was used as the electron-transport layer. LiF/Al was used as the cathode.

OLEDs were fabricated by deposition of the organic layer onto a cleaned glass substrate pre-coated with ITO *via* thermal evaporation under vacuum without breaking the vacuum. Prior to organic layer deposition, the ITO substrates were exposed to a UV-ozone flux for 10 min following degreasing with acetone and isopropyl alcohol. All organic layers were grown by thermal evaporation at a base pressure of $< 1 \times 10^{-7}$ Torr. The OLED current density-voltage-luminescence (J-V-L) characteristics were measured simultaneously using a Keithley 2400 programmable source meter and SpectraScan PR650 (Photo Research) instrument.

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