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1*H*-Pyrazolo[3,4-b]quinolines and Their Performance in Electroluminescent Devices

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A series of highly luminescent pyrazolo[3,4-b]quinolines were prepared and used as luminophores in fabrication of three-layer electroluminescent devices. The devices were fabricated using the basic structure of indium tinoxide (ITO)/TPD/Pyrazoloquinoline/ALQ/Mg:Ag, where TPD (3-methylphenyl)-1,1′-biphenyl-4,4′-diamine was used as a hole transport layer and AlQ (8-hydroxyquinoline) as an electron transport layer. Bright blue-green and blue emissions were obtained from all the devices with such configurations. The devices with **6d** and **6f** pyrazoloquinoline derivatives achieved L_{max} = 20800 cd/m^2 and 8550 cd/m^2 at a current density of 30 mA/4 mm^2. The luminance efficiency was 3.38 and 1.70 lm/W respectively.

Key words: blue emission, blue-green emission, fluorescence, luminophores, three-layer electroluminescent cells

In recent years, organic compounds suitable for the blue-emitting electroluminescent devices (EL) evoked a great interest [1–3]. Number of syntheses has been developed and a number of compounds prepared. Particular attention has been paid to azaheterocyclic compounds, among them pyrazoles [4–7], benzoxazoles [8,9], triazoles [10], oxadiazoles [11], and quinoxaline [12]. Because recently prepared 1*H*-pyrazolo[3,4-b]quinolines (PQ) exhibited strong luminescence in blue to green region in solution and in the solid state [13,14] they might be right luminophores for EL devices. Since their first preparation [15] compounds belonging to this class attracted attention mainly as interferon inducers [16,17]. In our recent studies 1H-pyrazolo[3,4-b]pyrazolo quinolines have been demonstrated as useful components of EL [18–20], dopants in poly(vinylcarbazole) [21] and co-polymers with vinylcarbazole and polyesters [22] used in EL.

In this paper application of a series of newly prepared, blue-light emitting PQ (**6**) as luminophores in vacuum deposited, three-layered EL is presented. Preliminary report was published [23]. The luminophores were prepared by thermal condensation of aromatic amines with 1,3-disubstituted-5-chloro-4-formylopyrazoles (Table 1). Elucidation of the emission mechanism of the three-layered EL with these luminophores is attempted.

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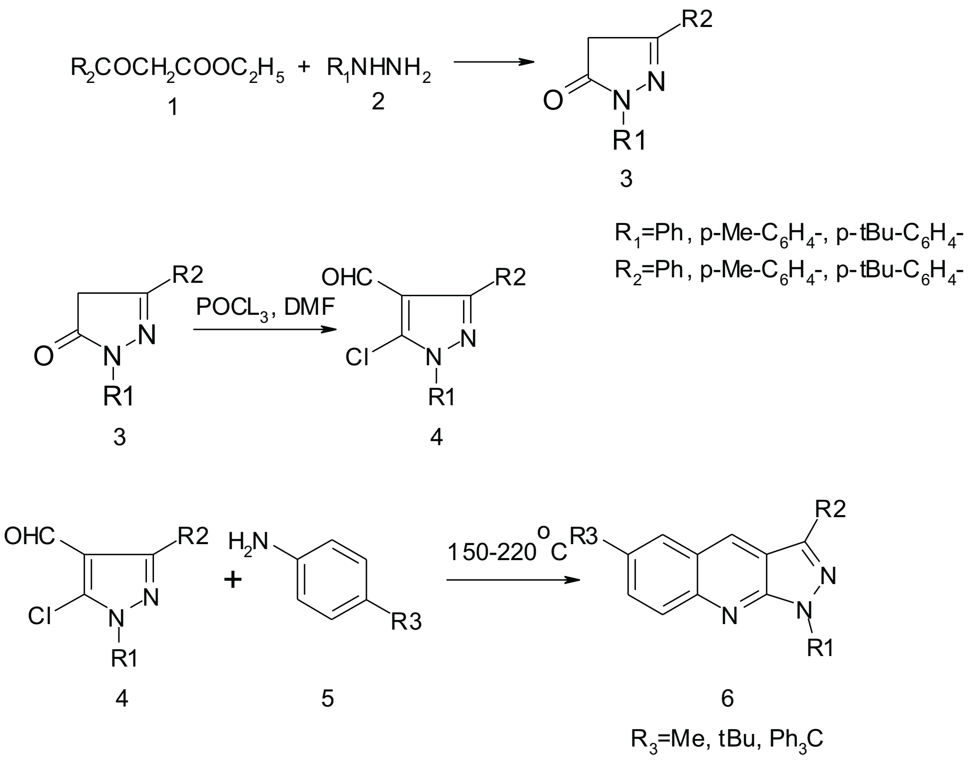
Table 1. 1*H*-*P*yrazolo[3,4-b]quinolines (PQ) (**6**) used in the EL fabrication.

PQ	R_1	R_2	R_3	T.t.°C
6a	Ph	Ph	H	167
6b	p-Me-C_6H_4	p-Me-C_6H_4	*tert*-Bu	206
6c	p-Me-C_6H_4	p-*tert*-Bu-C_6H_4	*tert*-Bu	201
6d	Ph	Ph	NPh_2	232
6e	p-*tert*-Bu-C_6H_4	p-*tert*-Bu-C_6H_4	*tert*-Bu	163
6f	Ph	Ph	CPh_3	301
6g	p-Me-C_6H_4	p-*tert*-Bu-C_6H_4	CPh_3	332
6h	Me	Ph	CPh_3	275

EXPERIMENTAL

Syntheses. The synthesis of pyrazolo[3,4-b]quinolines is outlined on the Scheme 1.

Scheme 1



Pyrazolin-5-ones (3) (A general procedure).

A β-ketoester **1** (0.1 mole) with hydrazine **2** (0.1 mole) and were refluxed in ethanol (50 ml) for 60 min. After cooling the precipitate was filtered off, washed with diethyl ether and dried.

1,3-di-(p-Toluyl)-pyrazolin-5-one (**3a**). Light yellow crystals, 67%, m.p. 114–115°C. Anal. Calcd for $C_{17}H_{16}N_2O$ (264.33): C, 77.25; H, 6.10; N, 10.60. Found: C, 77.16; H, 6.01; N, 10.74%.

1,3-(p-tert-Butylphenyl)-pyrazolin-5-one (**3b**). Colourless crystals, 55%, m.p. 198–199°C. Anal. Calcd for $C_{23}H_{28}N_2O$ (348.49): C, 79.27; H, 8.10; N, 8.04. Found: C, 79.15; H, 8.14; N, 7.89%.

3-(p-tert-Butylphenyl)-1-(p-methylphenyl)-pyrazolin-5-one (**3c**). Creamy plates; 60%, m.p. 152–153°C. IR (KBr): 1712 (CO). Anal. Calcd for $C_{20}H_{22}N_2O$ (306.41): C, 78.40; H, 7.24; N, 9.14. Found: C, 78.15; H, 7.11; N, 8.88%.

1,3-Disubstituted 5-chloro-4-formylopyrazoles (4) (A general procedure).

All the syntheses were made by Vilsmeier-Haack formylation of pyrazol-5-ones (**3**) according to Becher [24].

Phosphorus oxychloride (0.7 mol; 64 ml) was added dropwise ice cooled *N,N*-dimethylformamide (0.3 mole, 23 ml). To this Vilsmeier-Haack reagent pyrazolin-5-one (**3**) (0.1 mole) was added whereupon the reaction mixture was refluxed for 1 hour. After cooling the reaction mixture was poured on 600 ml ice/water mixture. The precipitated product was filtered, washed with water, dried, and recrystallized.

1,3-(p-Methylphenyl)-5-chloro-4-formylopyrazol (**4a**). Light yellow crystals, 75%, m.p. 123–4°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 10.06 (s, 1H, CHO); 7.78–7.87 (d, J = 8.2 Hz, 2H); 7.59–7.67 (d, J = 8.2 Hz, 2H); 7.18–7.25 (m, 4H); 2.38 (s, 3H, Me); 2.35 (s, 3H, Me). Anal. Calcd. for $C_{18}H_{15}ClN_2O$ (310.79): C 69.57; H 4.86; N 9.01. Found : C 69.45; H 4.54; N, 8.78.

1,3-(4’-tert-Butylphenyl)-5-chloro-4-formylopyrazol (**4b**). Colourless crystals, 65%, m.p. 167–9°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 10.06 (s, 1H, CHO); 7.53 (s, 4H, H-2’,3’,5’,6’); 7.48 (d, J = 8.2 Hz, 2H, H-3’,5’); 7.45 (d, J = 8.2 Hz, 2H, H-2,6); 1.38 (s, 9H, 4”-t-Bu); 1.36 (s, 9H, 4’-t-Bu). Anal. Calcd. for $C_{24}H_{27}ClN_2O$ (394.95): C, 72.99; H, 6.89; N, 7.09. Found: C, 72.76; H, 6.81; N, 7.25%.

3-(p-tert-Butylphenyl)-5-chloro-4-formylo-1-p-methylphenylpyrazol (**4c**). Light yellow crystals, 74%, m.p. 148–9°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm]: 10.06 (s, 1H, CHO); 7.75 (d, J = 8.5 Hz, 2H, H-2,6); 7.49 (d, J = 8.5 Hz, 4H, H-2’,3’,5’,6’); 7.33 (d, J = 8.2 Hz, 2H, H-3,5); 2.45 (s, 3H, 4-Me); 1.36 (s, 9H, 4’-t-Bu). Anal. Calcd. for $C_{21}H_{21}ClN_2O$ (352.87): C, 71.48; H, 6.00; N, 7.94. Found: C, 71.13; H, 6.19; N, 7.78%.

1H-Pyrazolo[3,4-b]quinolines (PQ) (6).

1*H*-Pyrazolo[3,4-b]quinolines (**6b–h**) were synthesized by thermal condensation of aromatic amines (**5**), this is, aniline, p-toluidine, p-(*tert*-butyl)-aniline, p-(triphenylmethyl)aniline and p-(N,N-diphenyl)-aniline with 5-chloro-4-formylpyrazoles (**4**) according to Brack [25].

1,3-Diphenylo-1H-pyrazolo[3,4-b]quinoline (**6a**) was prepared according to Tomasik *et al*. [26].

6-tert-Butyl-1,3-di(p-toluyl)-1H-pyrazolo[3,4-b]quinoline (**6b**). Bright yellow crystals, 96%, m.p. 206–207°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm]: 8.9 (s, 1H, H-4); 8.50–8.40 (d, J = 8.1 Hz; 2H, H-2’,6’); 8.18–8.05 (d, J = 8.2 Hz, 2H, H-2”,6”; d, J = 9.2 Hz, 1H, H-8); 7.95–7.85 (s, 1H, H-5; d, J = 1Hz, H-7); 7.45–7.35 (m, 4H, H-3’,5’,3”,5”); 2.45 (s, 3H, 4’-Me); 2.48 (s, 3H, 4”-Me); 1.48 (s, 9H, 6-t-Bu). Anal. Calcd. for $C_{28}H_{27}N_3$ (405.55): C, 82.93; H, 6.71; N, 10.36. Found: C, 82.76; H, 6.64; N, 10.48%.

6-tert-Butyl-1-(p-toluyl)-3-(p-tert-butylphenyl)-1H-pyrazolo[3,4-b]quinoline (**6c**). Yellow crystals, 88%, m.p. 201–2°C. ^{1}H NMR (500 MHz; $CDCl_3$): δ [ppm]: 8.9 (s, 1H, H-4); 8.45 (d, J = 8.2 Hz, 2H, H-2’,6’); 8.20–8.08 (d, J = 8.2 Hz, H-2”,6”); 7.95–7.85 (s, 1H, H-5; d, J = 9.1 Hz, 1H, H-7); 7.65 (d, J = 8.5 Hz, 2H, H-3’,5’); 7.4 (d, J = 8.5 Hz, 2H, H-3”,5”); 1.42 (s, 9H, 4”-t-Bu); 2.45 (s, 3H, 4’-Me). Anal. Calcd. for $C_{31}H_{33}N_3$ (447.60): C, 83.18; H, 7.43; N, 9.39. Found: C, 83.01; H, 7.25; N, 9.31.

1,3-Diphenyl-6-N,N-diphenylamino-1H-pyrazolo[3,4-b]quinoline (**6d**).Yellow crystals, 53%, m.p. 232–4°C. ^{1}H NMR (500 MHz; $CDCl_3$): δ [ppm]: 8.63 (s, 1H, H-5); 8.43 (d, J = 9.21 Hz, 2H, H-2’,6’); 8.04 (d, J = 8.06 Hz, 1H, H-8); 8.03 (d, J = 7.0 Hz, 2H, H-2”,6”); 7.59 (d, J = 6.84 Hz, 2H); 7.56 (d, J = 8.71 Hz, 2H); 7.51 (d, J_{H7-H5} = 2.45 Hz, 1H, H-5); 7.30 (t, J = 7.88 Hz, 2H, H-2”,6”); 7.18 (d, J = 7.6 Hz, 4H, H-2,$6_{N,N-Ph}$); 7.08 (t, J = 7.3 Hz, 2H, H-$4_{N,N-Ph}$); 1.39 (s, 9H, 4”-t-Bu); 1.38 (s, 9H, 4’-t-Bu). Anal. Calcd. for $C_{34}H_{24}N_4$ (488.60): C, 83.58; H, 4.95; N, 11.47. Found: C, 83.42; H, 4.87; N, 11.32%.

6-tert-Butyl-1,3-(p-tert-butylphenyl)-1H-pyrazolo[3,4-b]quinoline (**6e**). Yellow crystals, 77%, m.p. 163–4°C. ^{1}H NMR (500 MHz, CDCl$_3$): δ [ppm]: 8.84 (s, 1H, H-5); 8.47–8.45 (d, 2H); 8.10–8.06 (m, 3H); 7.87–7.86 (m, 2H); 7.58–7.57 (m, 4H); 1.44 (s, 9H, 6-t-Bu); 1.40 (s, 18H, 6Me);. Anal. Calcd. for $C_{34}H_{39}N_3$ (489.71): C, 83.39; H, 8.03; N, 8.58. Found: C, 83.14; H, 8.21; N, 8.31%.

1,3-Diphenyl-6-triphenylmethyl-1H-pyrazolo[3,4-b]quinoline (**6f**). Yellow crystals, 89%, m.p. 301–302°C. ^{1}H NMR (500 MHz, CDCl$_3$): δ [ppm]: 8.77 (s, 1H, H-4); 8.55 (d, J = 8.5 Hz, 2H, H-2’,6’); 8.12 (d, J = 7.07 Hz, 2H, H-2”,6”); 8.00 (d, J = 9.17 Hz, 1H, H-8); 7.90 (d, J = 2.15 Hz, 1H, H-5); 7.57–7.53 (m, 5H, H-7, H-3’,5’,3”,5”); 7.46 (t, J = 7.41 Hz, 1H, H-4’); 7.31–7.26 (m, 13 H, H-4”,12H$_{trityl}$, H-2,3,4,5); 7.24 (t, J = 7.35 Hz, 3H$_{trityl}$, H-4). Anal. Calcd. for $C_{41}H_{29}N_3$ (563.71): C, 87.36; H, 5.19; N, 7.45. Found: C, 87.24; H, 4.98; N, 7.32%.

3-(p-tert-Butylphenyl)-1-p-toluyl-6-triphenylmethyl-1H-pyrazolo[3,4-b]quinoline (**6g**). Yellow crystals, 76%, m.p. 332°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ [ppm]: 8.76 (1H, H-4); 8.42 (d, J = 8.5 Hz, 2H); 8.04 (d, J = 8.2 Hz, 2H); 7.99 (d, J = 9.3 Hz, 1H, H-8); 7.88 (d, J = 2.1 Hz, H-5); 7.58 (d, J = 8.5 Hz, 2H); 7.52 (dd, J = 9.2 Hz, 2.2 Hz; 1H, H-7); 7.38–7.20 (m, 15H); 2.44 (s, 3H, N-Me); 1.4 (s, 9H, t-Bu). Anal. Calcd. for $C_{46}H_{39}N_3$ (633.84): C, 87.17; H, 6.20; N, 6.63. Found: C, 87.01; H, 6.25; N, 6.75%.

1-Methyl-3-phenyl-6-triphenylmethyl-1H-pyrazolo[3,4-b]quinoline (**6h**). Light yellow crystals, 67%, m.p. 275–6°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ [ppm]: 8.71 (s, 1H, H-4); 8.18 (d, J = 7.1 Hz, 2H, H-2’,6’); 7.94 (d, J = 9.34 Hz, 1H, H-8); 7.53–7.48 (m, 3H, H-3’,5’); 7.41 (t, J = 7.1 Hz, 1H, H-4’); 7.30–7.20 (m, 15H, 6-Ph$_3$C); 4.27 (s, 3H, N-Me). Anal. Calcd. for $C_{36}H_{27}N_3$ (501.64): C, 86.20; H, 5.43; N, 8.38. Found: C, 86.11; H, 5.56; N, 8.24%.

EL fabrication. Glass substrates with 2 mm ITO lines and non-fluorescent glasses were used for the EL and PL experiments, respectively. They were cleaned with ultrasonication in pure water and subsequently in acetone and then dried under ethanol vapour. Thin layers of PQ derivatives on the non-fluorescent glass support were prepared by means of a vacuum deposition and thickness of the layer was determined (Dektak). The transparency of the layer was measured with a spectrophotometer (UV4500 Hitachi). Photoluminescence of the layer was measured using a fluorescence spectrophotometer (UV3000 Hitachi). Ionization potentials of PQ derivatives were determined by the photoelectron spectroscopy (AC-1 Rikenkeiki). The light brightness-current-voltage characteristics of the devices were measured using luminance meter (BM-8) and a source measure unit (Ketley model 236). Electroluminescent spectra were recorded at constant current of 1mA/4 mm^2 from a spectradiometer (SR-1 TOPCON).

The three-layer EL device was fabricated in course of successive depositions of *N,N′*-diphenyl-*N,N′*-(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), the PQ derivative and 8-hydroxyquinoline aluminium (AlQ) on the ITO glass substrates. As an alloy-type electrode, magnesium and silver were co-deposited with a volume ratio of 10:1. All of the vacuum depositions were carried out in the 10^{-6} Torr from tantalum boat using shadow masks and several shutters in a deposition apparatus. The deposition rates were monitored independently by thickness/rate monitors and were 5 Å/sec for all these organic compounds. The magnesium silver electrodes were prepared by simultaneous deposition from two different sources at the rates of about 20 and 2 Å/sec respectively. Light brightness – current-voltage characteristics of the devices were measured using a luminance meter and a source measurement unit. The electroluminescence spectra were obtained at the constant current of 1 mA/4 mm^2.

RESULTS AND DISCUSSION

Emission from 1,3-diphenyl-1*H*-pyrazolo[3,4-b]quinoline (PQ-**6a**) in 1,4-dioxane, the first ever tested PQ showed a strong blue emission at 463 nm. The same emission was recorded in ethanol. This luminophore was applied in a two-layer EL device. A TPD layer served for a hole-transport and PQ **6a** was embedded in a hole-transport layer of Bu-PBD by means of a co-deposition. The device showed the blue emission at 470 nm upon application of approximately 10 V DC at specified current density, which was entirely due to the emission from PQ-**6a**. However, the emission intensity reached no more than 20 cd/m^2. In the case of low content of PQ-**6a** in the Bu-PBD layer the emission at 400 nm was observed which originated from Bu-PBD.

A subsequent three-layer EL device was fabricated where the PQ-**6a** layer was sandwiched with electron-transport and a hole-transport layers. An increase in the thickness of the PQ-**6a** layer increased the emission intensity up to almost 100 cd/m^2. However, the thicker layers shifted emission to the greenish region, this is, to 530 nm. Apparently, this effect might result from the excimer emission from PQ-**6a**. However, result of the measurements for concentrated solution and solid state of PQ-**6** did not support this supposition. Therefore, assumption of Amemiya *et al.* [27] was followed to rationalize observed behaviour of that luminophore. Thus, the effect resulted from interference of the light with the metal electrode.

In order to avoid crystallization during deposition of the PQ film bulky substituents such as triphenylmethyl, *tert*-butyl, *tert*-butylphenyl, methylphenyl, and diphenylamino groups were attached into the PQ backbone. All these PQ derivatives produced stable, and smooth vacuum-deposited films. All these derivatives, except PQ-**6a** and PQ-**6e**, melted above 200°C. Emission peaks in their photoluminescence spectra and the ionization potentials of the thin layers of PQs are summarized in Table 2.

There is a rough correlation between the wavelength of emission and electron affinities, E_a. PQ-**6h** emitting the shortest wavelength light indicated the highest E_a and PQ-**6d** emitting the longest wavelength light showed the lowest E_a. Generally, changes in E_a are not too sensitive to changes in emission wavelength. There is no correlation between emission wavelength and ionization potential, I_p.

Table 2. Emission peaks Em, electron affinities E_a and ionisation potentials I_p of PQs thin layers.

PQ	Em(nm)	E_a(eV)	I_p(eV)
6b	490	2.59	5.60
6c	495	2.59	5.50
6d	520	2.38	5.55
6e	490	2.69	5.50
6f	479	2.69	5.70
6g	495	2.59	5.60
6h	455	2.73	5.70

The thin layers made of PQ derivatives emitted blue to green light depending on the substituents.

Within the utilized range of measurements luminance was proportional to the current density. The luminance efficiency was 0.95 lm/W at the brightness of 100 cd/m^2, the emission peak appeared at 475 nm and the spectra were identical to the photoluminescence of the thin layer.

The electroluminescent characteristics of the three-layer EL fabricated with other PQs were taken following procedure for PQ-**6f**. These characteristics are summarized in Table 3. The electroluminescence spectra of these PQs were similar to their photoluminescence spectra (Table 3).

Table 3. The characteristics of EL devices of type TPD(500Å)/PQ(×Å)/AlQ(300Å)/MgAg.

PQ	x(Å)[a]	λ_{em}(nm)[b]	CIEx[c]	CIEy[d]	ϕe(%)[e]	η(lm/W)[f]
6b	185	495	0.19	0.45	1.22	1.85
6c	154	490	0.17	0.40	1.06	1.20
6d	154	525	0.28	0.63	0.89	1.89
6e	170	500	0.18	0.43	0.67	1.07
6f	153	475	0.16	0.30	0.66	0.71
6g	170	490	0.17	0.43	0.98	1.35
6h	170	465	0.17	0.23	0.41	0.43

[a] The emission layer thickness.
[b] The wavelength of the emission peak at I = 1 mA/4 mm^2.
[c] The chromacity coordinates along the x-axis,
[d] The chromacity coordinates along the y-axis.
[e] The external quantum efficiency (EQE).
[f] The luminance efficiency.

The highest luminance efficiency of these PQ derivatives was 1.89 lm/W at the current density of 1 mA/4 mm^2 for the EL with PQ-**6d** but the external quantum efficiency was below 1% because of the lower energy green emission. Coordinates in the chromacity diagram (CIE) [28] for the device with PQ-**6h** were the lowest and the luminance efficiency was 0.43 lm/W. The highest external quantum efficiency (EQE) of 1.22% was measured for the device with PQ-**6b**. (EQE is defined as the product of internal quantum efficiency and light extraction efficiency [27]). It emitted the blue-green light. Maximum brightness was observed for the devices based on PQ-**6d** and PQ-**6f** at 20800 and 8550 cd/m^2 respectively. The luminance efficiency was 3.62 and 1.24 lm/W respectively. The external quantum efficiency was 1.19 and 1.13 % for these PQ derivatives. Comparison of the data for electroluminescence of PQ in EL devices (Table 3) with the data for photoluminescence of those PQ in the solid state revealed that the differences in the emission wavelengths varied for particular PQ by not more than 10 nm, usually by 5 nm. There is no clear relationship between structure and direction of the shift in particular kind of luminescence.

The wavelength of emission from the device was also modified by the thickness of the emission layer (Table 4). As the thickness of the emission increased the colour of emission shifted from blue to green and the spectral width also increased.

Table 4. The characteristics of a [TPD(500Å)/PQ-6f(×Å)/AlQ(300Å)/MgAg] EL with emission layers of different thickness (x)[a].

x(Å)	λ_{em}(nm)	CIEx	CIEy	ϕe(%)	η(lm/W)
102	470	0.17	0.28	0.55	0.68
153	475	0.16	0.30	0.66	0.71
178	480	0.16	0.32	0.76	0.83
191	475	0.16	0.30	0.75	0.87
229	485	0.16	0.32	0.72	0.77
306	490	0.18	0.38	0.74	0.73
459	505	0.22	0.44	0.53	0.54
612	505	0.25	0.45	0.45	0.38

[a]The meaning of symbols in the Table heading are the same as in Table 3.

The observed spectral change due to the emission-layer thickness could be rationalized in terms of the model of Amemiya *et al.* [27] based on the interference of the light from the metal electrode. In this model output of the emission was affected by two factors. They are the interference effect between a direct light from the metal electrode and the emitting-site distribution in the emission layer.

In conclusion, a novel 1H-pyrazolo[3,4-b]quinoline system was used to prepare the triple layered EL device. Bright blue-green light with the maximum luminance of 20800 cd/m^2 was observed at the drive current density of 30 mA/4 mm^2. We expect that further improvement in the molecular design of PQs will contribute to the fabrication of higher performance EL devices.

In the first experiment of Tsutsui *et al.* [29] with the blue emitter, the best device based on 1,1,4,4-tetraphenyl-1,3-butadiene gave a luminance of 700 cd/m^2 at a current of 100 mA/cm^2 by applying a dc voltage of 10 V. A luminance efficiency of 0.22 lm/W was estimated. The Tanaka [30] devices based on metal-chelate emitting materials (pyridine, benzoxazole and benzoimidazole derivatives) exhibited maximum luminance of 400–3000 cd/m^2 with luminance efficiency of 0.08–0.45 lm/W. The characteristics of blue organic electroluminescence in the device fabricated by Lee [5] with 1,3,5-triaryl-2-pyrazolines applied in two-layer EL devices provided brightness varying from 441 to 682 cd/m^2 with the luminance efficiency of 0.9–1.3 lm/W. The maximum luminance of EL device based on lithium tetra-(2-methyl-8-hydroxy-quinolinato) boron was 6900 cd/m^2 with the luminance efficiency of 1.3 lm/W [31]. Thus, one could conclude that the pyrazolo[3,4-b]quinolines can compete with other luminophores for EL devices.

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