JOURNAL OF
Materials
CHEMISTRY

Pyrazoloquinoline derivatives as efficient blue electroluminescent materials

Y. T. Tao,*[a] E. Balasubramaniam,[a] A. Danel,[b] A. Wisla[b] and P. Tomasik*[b]

[a]*Institute of Chemistry, Academia Sinica, Taipei, Taiwan, 11529, Republic of China*
[b]*Department of Chemistry, University of Agriculture, 31 129 Cracow, Poland*

Received 2nd October 2000, Accepted 1st December 2000
First published as an Advance Article on the web 5th February 2001

A series of 6-substituted-3-methyl-1-phenyl-4-(4-methoxyphenyl)-1*H*-pyrazolo[3,4-*b*]quinolines, MeOPAQ-X (X = *t*-Bu, OMe, H, F, Cl, Br), were synthesized and assessed as potential emitters in electroluminescent (EL) devices. All derivatives emitted in the blue region with an emission λ_{max} ranging from 448 nm to 460 nm and a quantum yield between 0.55 and 0.20. EL devices with a configuration of ITO/NPB/CBP/TPBI:MeOPAQ-X/TPBI/Mg:Ag were fabricated, where ITO, NPB, CBP, TPBI and Mg:Ag are indium tin oxide, 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl, 4,4′-dicarbazolyl-1,1′-biphenyl, 2,2′,2″-(benzene-1,3,5-triyl)tris[1-phenyl-1*H*-benzimidazole] and magnesium : silver alloy (~ 10 : 1) respectively. Light emission from the dopant was observed. An external quantum efficiency around 3% could be obtained for all substituted derivatives. In particular, brightness around 13 000 cd m^{-2} was achieved for the device based on MeOPAQ-H. The performances were comparable to the best available materials in the blue organic light-emitting diodes.

Introduction

Organic light-emitting diodes (OLEDs) hold technological promise for the development of low cost displays and emissive products.[1] Although much progress has been made over the past several years, the search for new materials with high luminescent efficiency and stability is still going on, in addition to the development of ingenious fabrication techniques for the devices. For making a full color display, various color emissions are needed, in particular, the primary red, green and blue. Among the efforts to achieve different colors, well over 100 000 cd m^{-2} in brightness with high external quantum efficiency can be achieved for green emission by doping of either fluorescent or phosphorescent derivatives.[2] Highly efficient blue and red emissions are still being sought.[3] The blue color is of particular interest partly because inorganic blue LEDs are rare[4] and partly because blue LEDs can be used to achieve green and red color emission by several pathways like dopant emission or fluorescent down-conversion.[5] Recent progress gave blue emitting OLEDs with a maximum brightness of ~ 10 000 cd m^{-2} and external quantum efficiency around 3%.[6] Pyrazole-containing derivatives are useful blue dyes,[7] some of which have been demonstrated to be blue emitters in electroluminescent (EL) devices.[8] We have developed a series of pyrazoloquinoline derivatives which give bright blue EL emission.[9] We hereby report a new series of pyrazoloquinoline derivatives, 6-substituted-3-methyl-1-phenyl-4-(4-methoxyphenyl)-1*H*-pyrazolo[3,4-*b*]quinolines, MeOPAQ-X (structure shown in Fig. 1) as blue emitters in electroluminescent fabrication. When used as a dopant in a device of structure ITO/NPB/CBP/TPBI:dopant/TPBI/Mg:Ag, where ITO, NPB, CBP, TPBI and Mg:Ag are indium tin oxide, 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]-biphenyl, 4,4′-dicarbazolyl-1,1′-biphenyl, 2,2′,2″-(benzene-1,3,5-triyl)tris[1-phenyl-1*H*-benzimidazole] and magnesium : silver alloy (~ 10 : 1) respectively, bright blue emission from the dye dopant was observed. The performance of the devices is discussed.

Experimental

Synthesis of MeOPAQ-X dyes

All MeOPAQ-X (X = *t*-Bu, OMe, H, F, Cl, Br) materials were synthesized following a general procedure shown in Scheme 1, as modified from the literature procedure.[10] Only the synthesis of 4-(*p*-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline (MeOPAQ-H) is described.

4-(*p*-Methoxyphenyl)-3-methyl-1-phenylpyrazol-5-one[10a]. A mixture of 3-methyl-1-phenylpyrazol-5-one (5.02 g, 0.029 mole) and calcium chloride (3.78 g, 0.05 mole) in dioxane (50 ml, 70 °C) was stirred while *p*-methoxyphenyl chloride (4.95 g, 0.029 mole) was slowly added. After addition the

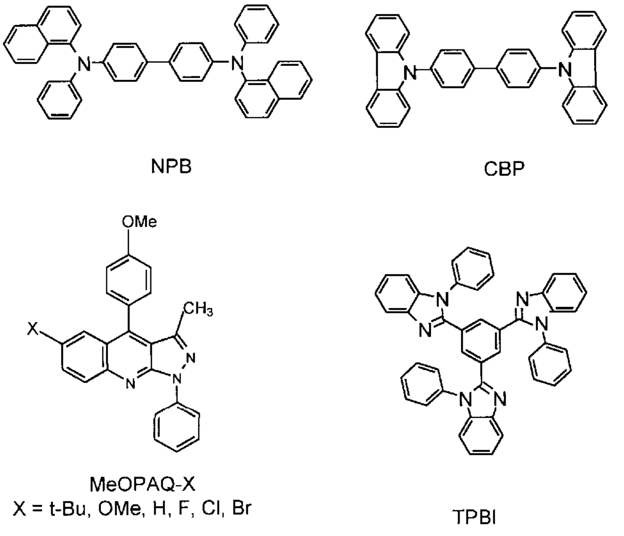
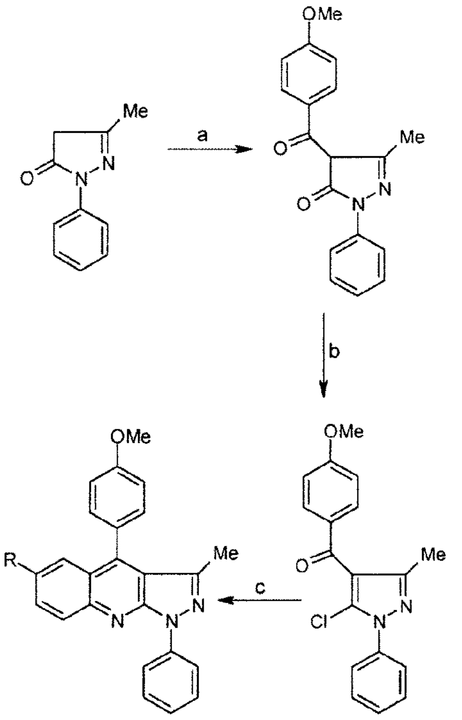


Fig. 1 The structure of OLED and MeOPAQ-X materials. The structures of hole-transporting (NPB; CBP) and electron-transporting host (TPBI) materials are also shown.



Scheme 1 *Reagents and conditions*: a) p-MeOC$_6$H$_4$COCl, dioxane, Ca(OH)$_2$, reflux, 4 h, 85%; b) POCl$_3$, 100 °C, 2 h, 96%; c) p-RC$_6$H$_4$NH$_2$, sulfolane, 220 °C, 3 h, 45–52%.

mixture was kept at 70 °C for 30 minutes followed by reflux for 4 hours. The resulting pink mixture was poured into ice-cold hydrochloric acid (2 M, 40 ml) and the beige crystals which were precipitated after one hour were isolated, 7.53 g (84%).

4-(p-Methoxyphenyl)-5-chloro-3-methyl-1-phenylpyrazole. 4-(p-Methoxyphenyl)-5-hydroxy-3-methyl-1-phenylpyrazole (3.77 g, 0.0122 mole) and phosphorus oxychloride (7.8 ml, 0.084 mole) were heated (110 °C) under reflux for 2 hours. After cooling the dark red mixture was poured into ice–water mixture and neutralized with 20% NaOH. The yellowish precipitate was collected and recrystallized from ethyl acetate to give beige needles in 96% yield, ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=2.20$ (s, 3H, 3-Me), 3.90 (s, 3H, OMe), 7.01 (d, $J=8.79$ Hz, 2H, H_{arom}), 7.42–7.58 (m, 5H), 7.84 (d, $J=8.8$ Hz, $2H_{arom}$).

4-(p-Methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline (MeOPAQ-H). 4-(p-Methoxyphenyl)-5-chloro-3-methyl-1-phenylpyrazole (0.01 mole), as prepared above, and 0.03 mole of aniline were heated together in 50 ml sulfolane at 220 °C for 3 h. After cooling, the reaction mixture was digested with water, acidified with diluted HCl and filtered off. The solid was subjected to column chromatography on aluminium oxide using CHCl$_3$ as the eluent to afford yellow needles in 45% yield, mp 205–207 °C. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=2.20$ (s, 3H, 3-Me), 3.95 (s, 3H, OMe), 7.12 (d, $J=8.5$ Hz, 2H, H_{arom}), 7.28 (t, $J=7.4$ Hz, 1H, H_{arom}), 7.32–7.40 (m, 3H, $H_{6,quinoline}$, 2H, H_{arom}), 7.58 (t, $J=8.5$ Hz, 2H, H_{arom}), 7.70–7.77 (m, 2H, $H_{5,7,quinoline}$), 8.18 (d, $J=8.51$ Hz, 1H, $H_{8,quinoline}$), 8.51 (d, $J=7.7$ Hz, 2H, H_{arom}). Anal. Calcd for C$_{24}$H$_{19}$N$_3$O: C, 78.88; H, 5.24; N, 11.50. Found: C, 79.08; H, 5.05; N, 11.56%.

6-Methoxy-4-(p-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline (MeOPAQ-OMe). Yellow crystals, 52%, mp 174–175 °C. ^{1}H NMR: $\delta=2.15$ (s, 3H, 3-Me), 2.15 (s, 3H, OMe), 3.93 (s, 3H, OMe), 6.93 (d, $J=3.02$ Hz, 1H, $H_{5,quinoline}$), 7.10 (d, $J=8.8$ Hz, 2H, H_{arom}), 7.25 (t, $J=7.4$ Hz, 1H, H_{arom}), 7.35–7.41 (m, 3H, $H_{7,quinoline}$, 2H, H_{arom}), 7.54 (t, $J=7.8$ Hz, 2H, H_{arom}), 8.05 (d, $J=9.34$ Hz, 1H, $H_{8,quinoline}$), 8.50 (d, $J=7.7$ Hz, 2H, H_{arom}). Anal. Calcd for C$_{25}$H$_{21}$N$_3$O$_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.86; H, 5.10; N, 10.63%.

6-*tert*-Butyl-4-(p-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline (MeOPAQ-*t*-Bu). Light yellow needles, 46%, mp 210–211 °C. ^{1}H NMR: $\delta=1.32$ (s, 9H, t-Bu), 2.19 (s, 3H, 3-Me), 3.96 (s, 3H, OMe), 7.12 (d, $J=8.5$ Hz, 2H, H_{arom}), 7.26 (t, $J=7.4$ Hz, 1H, H_{arom}), 7.39 (d, $J=8.51$ Hz, 2H, H_{arom}), 7.58 (t, 2H, H_{arom}), 7.67 (d, $J=1.9$ Hz, 1H, $H_{5,quinoline}$), 7.85 (dd, $J=9.0$, 1.9 Hz, 1H, $H_{7,quinoline}$), 8.12 (d, $J=9.0$ Hz, 1H, $H_{8,quinoline}$). Anal. Calcd for C$_{28}$H$_{27}$N$_3$O: C, 79.78; H, 6.46; N, 9.97. Found: C, 79.96; H, 6.24; N, 10.00%.

6-Bromo-4-(p-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline (MeOPAQ-Br). Yellow crystals, 51%, mp 182–183 °C. ^{1}H NMR: $\delta=2.12$ (s, 3H, 3-Me), 3.94 (s, 3H, OMe), 7.09 (d, $J=6.6$ Hz, 2H, H_{arom}), 7.26 (t, $J=7.4$ Hz, 1H, H_{arom}), 7.33 (d, $J=6.6$ Hz, 2H, H_{arom}), 7.53 (t, $J=8.5$ Hz, 2H, H_{arom}), 7.7 (dd, $J=9.1$, 2.2 Hz, 1H, $H_{7,quinoline}$), 7.83 (d, $J=2.2$ Hz, 1H, $H_{5,quinoline}$), 7.96 (d, $J=9.1$ Hz, 1H, $H_{8,quinoline}$), 8.46 (d, $J=7.7$ Hz, 2H, H_{arom}). Anal. Calcd for C$_{24}$H$_{18}$BrN$_3$O: C, 64.88; H, 4.08; N, 9.46. Found: C, 65.10; H, 3.92; N, 9.34%.

6-Chloro-4-(p-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline (MeOPAQ-Cl). Yellow crystals, 52%, mp 204–206 °C. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=2.17$ (s, 3H, 3-Me), 3.96 (s, 3H, OMe), 7.11 (d, $J=8.8$ Hz, 2H, H_{arom}), 7.27 (t, $J=7.4$ Hz, 1H, H_{arom}), 7.35 (d, $J=8.8$ Hz, 2H, H_{arom}), 7.55 (t, $J=7.4$ Hz, 2H, H_{arom}), 7.64 (dd, $J=9.1$, 2.4 Hz, 1H, $H_{7,quinoline}$), 7.70 (d, $J=2.2$ Hz, 1H, $H_{5,quinoline}$), 8.09 (d, $J=9.1$ Hz, 1H, $H_{8,quinoline}$), 8.45 (d, $J=7.4$ Hz, 2H, H_{arom}). Anal. Calcd for C$_{24}$H$_{18}$ClN$_3$O: C, 72.09; H, 4.54; N, 10.51. Found: C, 72.33; H, 4.40, N, 10.39%.

6-Fluoro-4-(p-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline (MeOPAQ-F). Yellow crystals, 47%, mp 184–186 °C. ^{1}H NMR (300MHz, CDCl$_3$): $\delta=2.17$ (s, 3H, 3-Me), 3.94 (s, 3H, OMe), 7.10 (d, $J=8.5$ Hz, 2H, H_{arom}), 7.27 (t, $J=7.4$ Hz, 1H, H_{arom}), 7.30–7.40 (m, 3H, $2H_{arom}$, $H_{7,quinoline}$), 7.46–7.60 (m, 3H, $2H_{arom}$, $H_{5,quinoline}$), 8.15 (dd, $J=9.3$, 5.5 Hz, 1H, $H_{8,quinoline}$), 8.47 (d, $J=7.4$ Hz, 2H, H_{arom}). Anal. Calcd for C$_{24}$H$_{18}$FN$_3$O: C, 75.18; H, 4.73; N, 10.96. Found: C, 75.20; H, 4.55; N, 10.87%.

The 4,4-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB), 4,4′-dicarbazolyl-1,1′-biphenyl (CBP) and 2,2′,2″-(benzene-1,3,5-triyl)tris[1-phenyl-1*H*-benzimidazole] (TPBI) were synthesized as described previously and purified by train sublimation.[8c]

Device fabrication

The general instrumentation and device fabrication are the same as that of our previous studies.[8c] Briefly, the ITO/NPB(20 nm)/CBP(20 nm)/TPBI:MeOPAQ-X(42 nm)/TPBI-(8 nm)/Mg:Ag devices were fabricated by physical vapor deposition of materials on a cleaned indium tin oxide-coated glass (effective area of a sample was 3.14 mm^2) at reduced pressure (10^{-6} Torr). The concentration of the dopant was maintained at ~2% (w/w) and the rate of deposition was maintained at 0.3–0.5 nm. The device performance was measured using a Keithley 2400 Source meter and a Newport 1835C Optical meter equipped with a Newport 818-ST silicon photodiode at an ambient condition, whereas the absorption, emission and differential scanning calorimetry experiments were done using Hewlett Packard 8453 absorption, Hitachi F-4500 fluorescence spectrophotometers, and Perkin–Elmer DSC7 differential scanning calorimeter respectively.

Table 1 Thermal and spectral properties of MeOPAQ derivatives. The absorption and emission spectra were measured in neat ethyl acetate. ~390 nm light was used as an excitation source for obtaining emission spectra. The relative quantum yield (ϕ) was measured with reference to 7-diethylamino-4-methylcoumarin[16]

	t-Bu	OMe	H	F	Cl	Br
Formula	$C_{28}H_{27}N_3O$	$C_{25}H_{21}N_3O_2$	$C_{24}H_{19}N_3O$	$C_{24}H_{18}FN_3O$	$C_{24}H_{18}ClN_3O$	$C_{24}H_{18}BrN_3O$
Molecular weight	421.55	395.47	365.44	383.43	399.88	444.33
T_m/°C[a]	207	173	202	185	179	200
T_g/°C[b]	62.6	53.6	38.1	NA	NA	NA
T_c/°C[c]	122.4	138.6	94.1	NA	NA	NA
Absorption peaks/nm	278, 312, 327, 393	276, 316, 331, 395(sh), 411	277, 312, 325, 392	272, 311, 324, 398	276, 316, 327, 399	276, 316, 326, 398
$\varepsilon_{376\ nm}$/M^{-1} cm^{-1}	4352	3066	6064	3754	3556	3754
Emission peak/nm	448	452	450	460	459	460
ϕ	0.52	0.55	0.53	0.42	0.41	0.20

[a] T_m: melting point. [b] T_g: glass transition temperature. [c] T_c: crystallization temperature.

Results and discussion

Table 1 summarizes the absorption and emission spectral data along with some thermal properties of the dyes. All derivatives have similar absorption patterns with a major absorption peak at around 390–400 nm (Fig. 2). The extinction coefficients are in the order of 10^4. These are ascribed to the π–π^* transition. The emissions are all in the blue region with the λ_{max} ranging between 448 nm and 460 nm, depending on the substituent. However, no systematic trend with respect to the electronic properties of the substituent can be discerned within this series. Reasonably high quantum yields ranging between 0.55 and 0.20 were observed, with the bromo-substituted one having the lowest value. The decreasing trend in quantum yield for the halogen-substituted derivative may relate to the heavy-atom effect within the molecule.[11] Most of the MeOPAQ-X materials melt near or around 200 °C. Among these, the MeOPAQ-X with X = H, MeO, and *t*-Bu show a glass transition temperature (T_g) above or around 40 °C. Only melting behavior was observed in the first heating cycle. After rapid cooling of the melt, the T_g was observed in the second heating cycle. Further heating resulted in crystallization of the respective compound at a higher temperature (T_c), which was followed by melting at the melting temperature T_m.[12] A higher T_g is a desirable material property in fabricating molecular LEDs, because a stable amorphous state of the deposited film is required. It is interesting to note that the molecular dipole moment vector, as calculated from molecular mechanics (PC Spartan Pro, version 1.05, from Wavefunction, Inc., Irvine, USA), is pointing along the long axis of the pyrazoloquinoline moiety for these derivatives, whereas for the three derivatives carrying electron-withdrawing substituent F, Cl and Br, the dipole moment vector points along the short axis of the pyrazoloquinoline moiety (Fig. 3). A correlation between T_g and thermal properties, such as entropy and enthalpy of fusion, for small organic molecules has been advanced.[13] Guidelines for designing organic glasses such as globular structure, large molecular weight and small intermolecular cohesion were proposed.[14] Yet the molecular dipole is another parameter that profoundly influences the packing of a material in the solid state. In the current case, the possible correlation between the direction of the dipole/structural features and the presence/absence of a T_g needs to be explored.

For device fabrication, four of the MeOPAQ-X derivatives, *i.e.* with X = methoxy, *tert*-butyl, hydrogen and fluoro were selected for the OLED fabrication. Due to the rather low T_g, these dyes may not have the morphological stability to serve as a pure emission layer. Nevertheless, doping into an appropriate host material will be considered. >From the analysis of emission/absorption spectra of TPBI[6] and the MeOPAQ dyes, reasonable spectral overlap and thus Forster energy transfer between TPBI and the dyes are expected. Our earlier work suggested that in device configuration ITO/NPB/TPBI/Mg:Ag, the TPBI serves as a hole blocker.[15] With an intermediate layer of CBP inserted between the NPB and TPBI layers, hole transport into the TPBI layer is enabled.[6] Thus the devices with a configuration of ITO/NPB(20 nm)/CBP(20 nm)/TPBI:2%-MeOPAQ-X(42 nm)/TPBI(8 nm)/Mg:Ag were fabricated. Bright blue electroluminescence (EL) on the forward bias was observed for all four dyes tested. The EL spectra are depicted in Fig. 4. The EL maxima show a substituent-

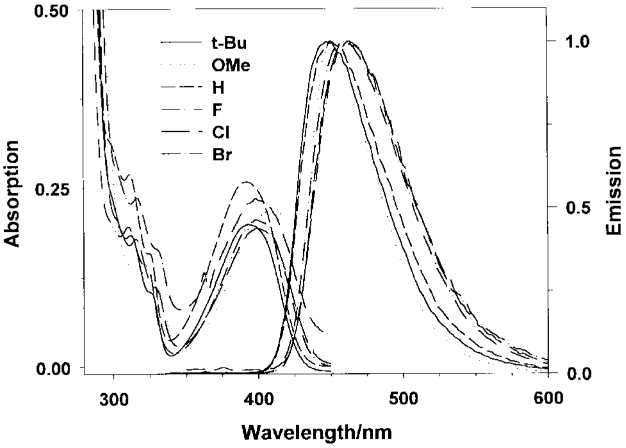


Fig. 2 Absorption and emission spectra of MeOPAQ derivatives in ethyl acetate. The emission spectra are normalized to each other for ease of comparison.

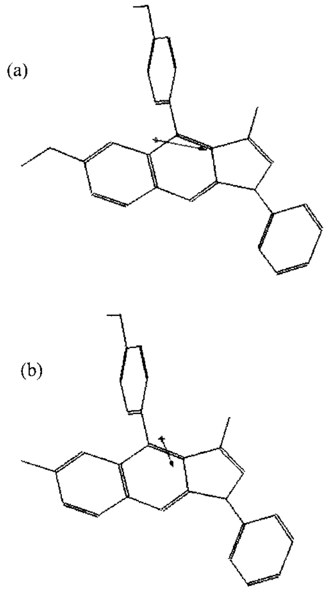


Fig. 3 The calculated molecular mechanics model display. (a) methoxy substituted MeOPAQ and (b) fluoro substituted MeOPAQ. The arrows indicate the dipole moment vector.

Table 2 Performance of the ITO/NPB/CBP/TPBI:MeOPAQ-X/TPBI/Mg:Ag devices under ambient conditions

	t-Bu	OMe	H	F
Turn-on voltage/V	4.4	4.4	4.3	4.5
Voltage/V^{a}	7.8	7.5	7.4	8.4
Brightness/cd m^{-2a}	680	651	957	845
Maximum brightness/cd m^{-2}	6434 at 13.5 V	5287 at 13.8 V	13 269 at 14 V	7187 at 15 V
External quantum efficiency (%)	3.22	3.12	3.44	3.12
Maximum quantum efficiency (%)	3.38 at 6.5 V	3.17 at 7.2 V	3.44 at 7.4	3.16 at 8.0 V
EL maximum/nm	442	454	454	458
CIE coordinates, *x* and *y*	0.17 and 0.11	0.17 and 0.12	0.19 and 0.16	0.19 and 0.17

[a]At 25 mA cm^{-2}.

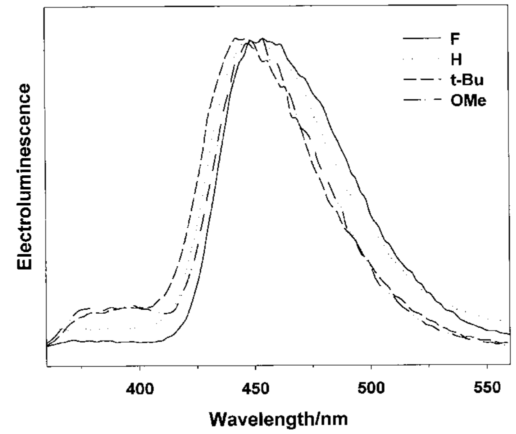


Fig. 4 The normalized electroluminescence spectra of ITO/NPB/CBP/TPBI:MeOPAQ-X/TPBI/Mg:Ag devices.

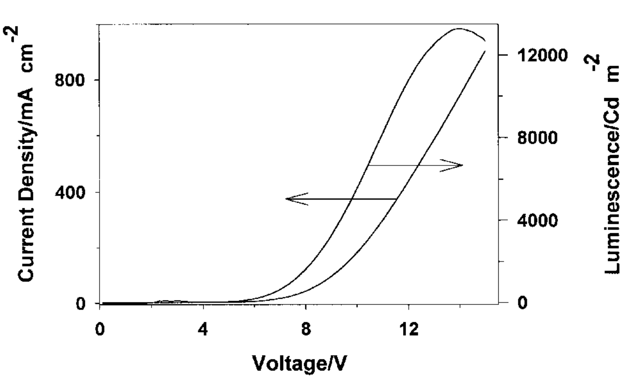


Fig. 5 The current–voltage luminescence characteristics of a ITO/NPB/CBP/TPBI:MeOPAQ-H/TPBI/Mg:Ag device.

dependence that is similar to that observed in the PL emission maxima of the same series, which implies the emission is indeed taking place from MeOPAQ-X derivatives. Presumably the charge recombination occurred in the TPBI layer and was followed by an energy transfer process from TPBI to the MeOPAQ-X dopant. In the case of methoxy- and *tert*-butyl-substituted dyes, a small shoulder below 400 nm was observed. The shoulder corresponds well to the emission of TPBI (378 nm). This can be an incomplete energy transfer between the host and the dopant under current conditions. A representative current–voltage luminescence characteristic is shown in Fig. 5. The EL peak maxima and Commission Internationale de L'Eclairage (CIE) coordinates of the light emission along with performance of the MeOPAQ-X based devices are summarized in Table 2. The device turn-on voltage is between 4.0 and 4.5 V. The luminance reaches as high as 13 500 cd m^2 in the case of MeOPAQ-H with a peak external quantum efficiency of 3.4%. Other substituents also have a similar performance but are less bright than MeOPAQ-H device. The device performance in general can not be correlated to the substituent as the molar absorption coefficient and the emission quantum yields (Table 1) do not follow a single trend. However, the present MeOPAQ-X materials are useful materials in the blue OLED category with a performance comparable to the best available materials.[6]

In conclusion, we have prepared and characterized a new series of pyrazoloquinoline derivatives, MeOPAQ-X, with various substituents. The absorption, emission and thermal studies revealed that the materials are suitable for blue OLED fabrication. The device ITO/NPB/CBP/TPBI:MeOPAQ-X/TPBI/Mg:Ag structure shows a bright blue EL which is again substituent dependent. The performance in terms of turn-on voltage, brightness and external quantum efficiency was demonstrated.

Acknowledgements

Financial support from Academia Sinica and the China Petroleum Corporation of the Republic of China and the Polish Research Council (Grant No. KBN 8T11B 075 18) are gratefully acknowledged.

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