

# Organic Light-Emitting Diodes Based on Variously Substituted Pyrazoloquinolines as Emitting Material

Y. T. Tao\* and E. Balasubramaniam

*Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, Republic of China*

A. Danel, B. Jarosz, and P. Tomasik\*

*Department of Chemistry, University of Agriculture, 31 129 Cracow, Poland*

*Received July 26, 2000. Revised Manuscript Received January 9, 2001*

1-Methyl-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinolines (PAQ) carrying various substituents at the 6- or 7-position (PAQ-X, X = OMe, *t*-Bu, H, F, CN, CF<sub>3</sub>, NEt<sub>2</sub>) were synthesized and studied as emitting materials in an organic light-emitting diode (OLED). The 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl ( $\alpha$ -NPB) and 4,4'-dicarbazolyl-1,1'-biphenyl (CBP) were used as hole-transporting materials, whereas electron-transporting 2,2',2''-(1,3,5-phenylene)-tris[1-phenyl-1*H*-benzimidazole] (TPBI) was used as a host for the PAQ-X dopant. The device with a general configuration of ITO/NPB/CBP/TPBI:PAQ-X/TPBI/Mg:Ag, where the PAQ-X dye concentration was kept around 2 wt %, was fabricated, and emits a bright blue light for all PAQ dyes except diethylamino-substituted PAQ, which emits blue-green light. With the same structure details, the electroluminescence, turn-on voltage, and external quantum efficiency show a dependence on the substitution. In particular, the external quantum efficiency and power efficiency are higher for devices doped with electron-rich PAQs and lower for electron-deficient PAQs.

## Introduction

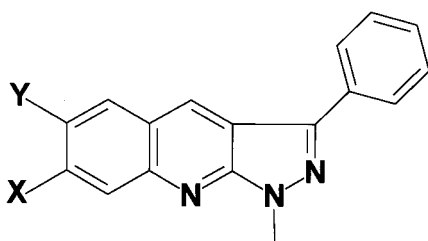
Since the initial work by Tang et al.<sup>1</sup> and Friend et al.<sup>2</sup> on light-emitting diodes (LED) using small organic molecules (OLED) and polymers (PLED), the LED research has attracted intense attention because of its application potential in flat panel displays.<sup>3</sup> The most actively pursued areas of research are the improvement of efficiency and stability (lifetime) of the device and the tuning of color using different emitting materials. The continuing efforts include ingenious device fabrication and synthesis of materials with improved properties.<sup>4</sup> In this context, molecules containing pyrazoline moiety have been explored for a variety of purposes. It is noted that some pyrazoline compounds are used in textile industry as optical brightener because of their high fluorescence yield and blue-light emission.<sup>5</sup> Pyrazolines

are also known as hole-transporting materials.<sup>6</sup> Sano et al.<sup>7</sup> have prepared a dimer of pyrazoline and used as hole-transporting material in OLED fabrication. Recently, a few pyrazoline derivatives were used in OLED as carrier-transporting as well as emitting materials.<sup>8</sup> Huang et al.<sup>9</sup> have prepared and used pyrene-substituted pyrazoline as an emitting material in OLED. Fu et al.<sup>10</sup> have demonstrated the optical size effect in pyrazoline nanocrystals that is useful for controlling wavelength in electroluminescent material. Several pyrazoline derivatives have also been studied in molecularly doped polymer LEDs.<sup>11</sup> Most recently, we have reported the use of dipyrazolopyridine derivatives as efficient blue light-emitting materials in multilayer OLED.<sup>12</sup> We have also reported the use of diethylamino-

- (1) Tang, C. W.; Vanslyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.  
 (2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.  
 (3) (a) Dodabalapur, A. *Solid State Commun.* **1997**, *102*, 259. (b) Gu, G.; Forrest, S. R. *IEEE J. Sel. Top. Quantum Electron.* **1998**, *4*, 83. (c) Dixon, R. *Compd. Semiconduct.* **1999**, *9*, 43. (d) Kido, J. *Phys. World* **1999**, *27*. (e) Ziemelis, K. *Nature* **1999**, *399*, 408.  
 (4) (a) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799. (b) Kido, J.; Kimura, M.; Nagai, K. *Science* **1995**, *267*, 1332. (c) *Organic Electroluminescent Materials and Devices*; Miyata, S., Nalwa, H. S., Eds.; Gordon and Breach Publishers: Amsterdam, 1997. (d) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161. (e) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 6698. (f) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1. (g) Wu, I. Y.; Lin, J. T.; Tao, Y. T.; Balasubramaniam, E. *Adv. Mater.* **2000**, *12*, 668. (h) Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10*, 1471.  
 (5) (a) Sandler, S. R.; Tsou, K. C. *J. Chem. Phys.* **1963**, *39*, 1062. (b) Yan, Z. L.; Hu, G. W.; Wu, S. K. *Acta Chim. Sin.* **1995**, *53*, 227.

- (6) (a) Borsenberger, P. M.; Schein, L. B. *J. Phys. Chem.* **1994**, *98*, 233. (b) Young, R. H.; Fitzgerald, J. J. *J. Phys. Chem.* **1995**, *99*, 4230.  
 (7) Sano, T.; Fujii, T.; Nishio, Y.; Hamada, Y.; Shibata, K.; Kuroki, K. *Jpn. J. Appl. Phys., Part 1* **1995**, *34*, 3124.  
 (8) (a) Gao, Z. Q.; Lee, C. S.; Bello, I.; Lee, S. T.; Wu, S. K.; Yan, Z. L.; Zhang, X. H. *Synth. Met.* **1999**, *105*, 141. (b) Zhang, X. H.; Lai, W. Y.; Gao, Z. Q.; Wong, T. C.; Lee, C. S.; Kwong, H. L.; Lee, S. T.; Wu, S. K. *Chem. Phys. Lett.* **2000**, *320*, 77. (c) Lu, Z.; Jiang, Q.; Zhu, W.; Xie, M.; Hou, Y.; Chen, X.; Wang, Z.; Zou, D.; Tsutsui, T. *Synth. Met.* **2000**, *111–112*, 425. (d) Lu, Z.; Jiang, Q.; Zhu, W.; Xie, M.; Hou, Y.; Chen, X.; Wang, Z. *Synth. Met.* **2000**, *111–112*, 465.  
 (9) Gao, X. C.; Cao, H.; Zhang, L. Q.; Zhang, B. W.; Cao, Y.; Huang, C. H. *J. Mater. Chem.* **1999**, *9*, 1077.  
 (10) Fu, H.-B.; Wang, Y.-Q.; Yao, J.-N. *Chem. Phys. Lett.* **2000**, *322*, 327.  
 (11) (a) He, Z.; Milburn, G. H. W.; Danel, A.; Puchala, A.; Tomasik, P.; Rasala, D. *J. Mater. Chem.* **1997**, *7*, 2323. (b) Danel, A.; Tomasik, P.; He, Z.; Milburn, G. H. W. *J. Mater. Chem.* **1999**, *9*, 339. (c) Tameev, A. R.; He, Z.; Milburn, G. H. W.; Kozlov, A. A.; Vannikov, A. V.; Danel, A.; Tomasik, P. *Appl. Phys. Lett.* **2000**, *77*, 322.  
 (12) (a) Balasubramaniam, E.; Tao, Y. T.; Danel, A.; Tomasik, P. *Chem. Mater.* **2000**, *12*, 2788. (b) Tao, Y. T.; Balasubramaniam, E.; Danel, A.; Tomasik, P. *Appl. Phys. Lett.* **2000**, *77*, 933.

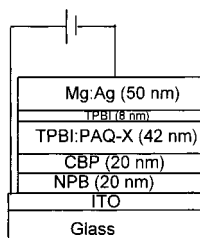
### Scheme 1. Structures of Substituted Pyrazoloquinolines and General Device Configuration



When X = H; Y = OMe, *t*-Bu, H, F, CN and NEt<sub>2</sub>

When Y = H; X = CF<sub>3</sub>

a



b

substituted pyrazoloquinoline (PAQ-NEt<sub>2</sub>) to give a sharp green electroluminescence.<sup>13</sup> In this report, we examine the property and performance of OLEDs based on variously substituted 1-methyl-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinolines (Scheme 1). All the new materials are emitting light in the blue region in contrast to the green emission from PAQ-NEt<sub>2</sub>. On the basis of this, the blue OLED was fabricated (Scheme 1). The details of thermal properties, electronic properties viz absorption and photoluminescence, electrochemical studies, device architecture, and the performance of the devices are discussed.

### Experimental Section

The pyrazoloquinoline (PAQ) derivatives were synthesized by modified literature procedures (see Supporting Information for details).<sup>14</sup> The electron-transporting material 2,2',2''-(1,3,5-phenylene)tris[1-phenyl-1*H*-benzimidazole] (TPBI) was prepared from benzene-1,3,5-tricarboxylic chloride and *N*-phenyl-1,2-phenylenediamine, followed by dehydration.<sup>15</sup> The TPBI was further purified by gradient sublimation twice. The hole-transporting materials 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl ( $\alpha$ -NPB) and 4,4'-dicarbazolyl-1,1'-biphenyl (CBP) were prepared via published methods and subjected to gradient sublimation prior to use.<sup>16</sup>

The thermal data were obtained from a Perkin-Elmer DSC7 differential scanning calorimeter. PAQ compounds were heated at 20 °C/min until complete melting and then cooled rapidly (quenching). A second heating scan at the same rate was performed to detect the glass transition temperature ( $T_g$ ), the crystallization temperature, and the melting temperature.<sup>16,17</sup> Absorption and emission measurements were carried out using a Hewlett-Packard 8453 absorption spectrophotometer and a

Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammetric experiments were done using a BAS 100B electrochemical analyzer. A conventional three-electrode cell system was used, with glassy carbon, platinum wire, and silver wire as the working, counter, and reference electrode, respectively. Degassed dichloromethane solution with 0.1 M tetrabutylammonium hexafluorophosphate was used as the solvent.

The substrate was an indium–tin oxide (ITO)-coated glass, with a sheet resistance of <50 ohms per square. The pretreatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. The thermal evaporation of organic materials was carried out using ULVAC Cryogenics at a chamber pressure of  $2 \times 10^{-6}$  Torr. The ITO/NPB/CBP/TPBI:PAQ-X/TPBI/Mg:Ag devices were fabricated with 20, 20, 42, and 8 nm thickness of NPB, CBP, TPBI:PAQ-X, and TPBI, respectively. For the doped TPBI:PAQ-X layer, the PAQ-X concentration was kept around 2 wt %, by coevaporating from a different thermal source with TPBI. The second layer of TPBI was used here to protect the luminescent layer from cathode deposition, where the penetration of hot metallic layer is expected in organic material for a few nanometers.<sup>18</sup> The cathode Mg<sub>0.9</sub>Ag<sub>0.1</sub> alloy was deposited (50 nm) by coevaporation. A thick layer (100 nm) of silver capping layer was finally deposited. The effective size of the emitting diode was 3.14 mm<sup>2</sup>. Current, voltage, and light intensity measurements ( $I$ – $V$ – $L$ ) were made simultaneously using a Keithley 2400 source meter and a Newport 1835C optical meter equipped with a Newport 818-ST silicon photodiode. The measurements were made at room temperature and ambient condition. The electroluminescence was measured using the fluorescence spectrophotometer with the incident light blocked from entering the sample compartment. For the necessary cases, a parallel deposition was carried out at the same time on a glass slide to measure the solid PL spectra.

### Results and Discussion

The thermal data of all PAQ materials are given in Table 1. In general, the melting points are ranging from 130 to 230 °C. The parent PAQ derivative (PAQ-H) exhibits a glass transition temperature ( $T_g$ ) around 32 °C. With a substituent at the 6- or 7-position, the  $T_g$  further decreased or was undetected. Following the  $T_g$ , a crystallization temperature  $T_c$  was usually observed before the melting of the sample.

The absorption spectra of PAQ materials in ethyl acetate are depicted in Figure 1. It is noted that, except for the methoxy-substituted and diethylamino-substituted PAQ (PAQ-OMe and PAQ-NEt<sub>2</sub>), a similar absorption pattern between 300 and 450 nm was observed for variously substituted PAQ derivatives. A small but definite substituent effect was observed such that electron-withdrawing groups (CN, CF<sub>3</sub>, and F) result in a red shift with respect to an electron-donating group (*t*-Bu). Nevertheless, for methoxy-substituted PAQ-OMe, a red shift and splitting of the 400 nm peak were observed. In the case of PAQ-NEt<sub>2</sub> an even more substantial red shift (>60 nm) was found. The concentration dependence study for PAQ-NEt<sub>2</sub> excludes the possibility of dimer or aggregation formation. The spectral shift in PAQ-NEt<sub>2</sub> and PAQ-OMe may be due to electronic effect, i.e., the mixing of lone pair orbital on the nitrogen/oxygen into the HOMO orbital.<sup>19</sup> Such a mixing is expected to raise the HOMO level and decrease the gap between HOMO and LUMO orbitals. Further, a similar absorption pattern for PAQ-CF<sub>3</sub> and

(13) Tao, Y. T.; Balasubramaniam, E.; Danel, A.; Jarosz, B.; Tomasik, P. *Appl. Phys. Lett.* **2000**, *77*, 1575.

(14) Brack, A. *Liebigs Ann. Chem.* **1965**, *681*, 105.

(15) Shi, J.; Tang, C. W.; Chen, C. H. U.S. Patent 5,645,948, 1997.

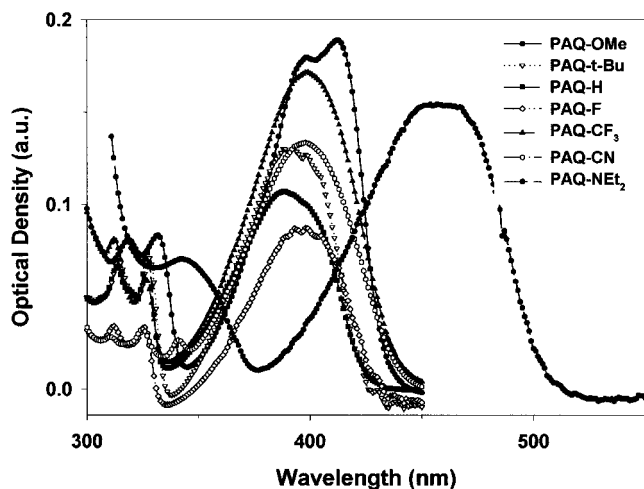
(16) Koene, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235.

(17) Naito, K.; Miura, A. *J. Phys. Chem.* **1993**, *97*, 6240.

(18) Lee, S. T.; Gao, Z. Q.; Hung, L. S. *Appl. Phys. Lett.* **1999**, *75*, 1404.

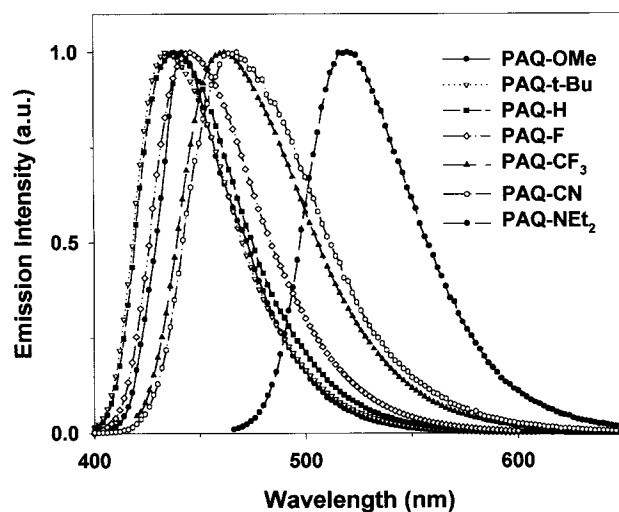
Table 1. Thermal and Spectral Characteristics of PAQ Materials

|                      | PAQ-OMe  | PAQ- <i>t</i> -Bu                              | PAQ-H  | PAQ-F  | PAQ-CF <sub>3</sub>   | PAQ-CN   | PAQ-NET <sub>2</sub>                           |
|----------------------|--|--|--|--|---|--|--|
| formula              | C <sub>18</sub> H <sub>15</sub> N <sub>3</sub> O | C <sub>21</sub> H <sub>21</sub> N <sub>3</sub> | C <sub>17</sub> H <sub>13</sub> N <sub>3</sub> | C <sub>17</sub> H <sub>12</sub> N <sub>3</sub> F | C <sub>18</sub> H <sub>12</sub> N <sub>3</sub> F <sub>3</sub> | C <sub>18</sub> H <sub>12</sub> N <sub>4</sub> | C <sub>21</sub> H <sub>22</sub> N <sub>4</sub> |
| mol wt               | 289.4  | 315.41   | 259.3  | 277.3  | 327.3   | 284.3  | 330.43   |
| melting point, °C    | 168  | 115  | 146  | 138  | 187   | 228  | 150  |
| T <sub>g</sub> , °C  | 30.3   | NA   | 31.9   | 17   | 7.7   | NA   | 18.1   |
| cryst temp, °C       | 84.7   | NA   | 54.3   | 68.6   | 78.4  | NA   | 94.2   |
| absorption peaks, nm | 319, 332, 392, 412                               | 314, 328, 388                                  | 313, 327, 388                                  | 312, 326, 398                                    | 312, 326, 399   | 310, 325, 398                                  | 342, 451                                       |
| emission peak, nm    | 442  | 434  | 438  | 446  | 462   | 468  | 521  |
| rel quantum yield    | 0.49   | 0.54   | 0.53   | 0.53   | 0.67  | 0.56   | 0.19   |



**Figure 1.** Absorption spectra of PAQ materials in ethyl acetate. Absorption was arbitrarily scaled relative to one another for ease in comparison.

PAQ-F suggests that the substituents at either 6- or 7-position of the quinoline moiety will have a similar effect on electronic transition. The photoluminescence (PL) spectra of PAQ materials are also measured in ethyl acetate, where the excitation of the samples was done at their respective absorption maximum. The normalized PL spectra are shown in Figure 2, and the peak positions are compiled in Table 1. The PAQ materials are emitting strongly in the blue region except for the PAQ-NET<sub>2</sub> emission, which is in the green region with  $\lambda_{\text{max}}$  around 521 nm. Among the blue-emitting PAQ materials, an electron-donating substituent (*tert*-butyl group<sup>20</sup>) shifts the emission spectra toward the high-energy region, whereas the electron-withdrawing substituents (CN, F, CF<sub>3</sub>) shift the same toward the low-energy region.<sup>21</sup> The relative quantum yield was measured with reference to 7-diethylamino-4-methylcoumarin (coumarin 1).<sup>22</sup> Excitation wavelength and optical density are kept the same for the standard and PAQ materials, while the area under the emission curve



**Figure 2.** Normalized emission spectra of PAQ materials in ethyl acetate solution. The PAQ-*t*-Bu, PAQ-F, and PAQ-CF<sub>3</sub> were excited using ~390 nm light, while PAQ-NET<sub>2</sub> was excited using 456 nm light.

and quantum yield of the standard are considered for calculating the relative quantum yield. Except for PAQ-NET<sub>2</sub>, which has a quantum yield of 0.19, all other materials have quantum yields greater than 0.5 (Table 1).

Multilayer OLED of the structure ITO/NPB/CBP/TPBI:PAQ-X/TPBI/Mg:Ag was fabricated. The TPBI was chosen as a host material for PAQ-X derivatives because it is a wide band gap material and emits strongly at around 376 nm,<sup>12b</sup> where most of the PAQ-X dyes have a very strong absorption (Figure 1). Two layers of hole-transporting material NPB and CBP were used as it was demonstrated previously that CBP serves to provide an intermediate HOMO level by which the holes can pass to the TPBI layer.<sup>12b,23</sup> In the absence of dopant, the ITO/NPB/CBP/TPBI/Mg:Ag device gave a broad electroluminescence (EL) spectrum that has a major contribution from TPBI (~380 nm) and a minor contribution from NPB (~450 nm) and possible emission from CBP, which occurs at around 390 nm.<sup>16</sup> This indicates that the recombination region located mainly in the TPBI region with some excitons occurred in the NPB area. In contrast, EL spectra of devices with 2% (w/w) PAQ-X doped into TPBI are blue. The emission maximum depends on the substituent X, shifted from the high-energy region to the low-energy region for electron-donating substituents to electron-withdrawing substituents, which is similar to that of solution PL of these PAQ materials. The normalized spectra are given in Figure 3, except for PAQ-NET<sub>2</sub>, which is green and will

(19) Using the Spartan properties package (Wavefunction Inc.), the HOMO-LUMO energy levels (highest occupied and lowest unoccupied molecular orbitals), and charge on substituents were assessed. (a) The electron densities for HOMO energy levels in lone-pair containing substituents (-NET<sub>2</sub> and -OMe) are lying in the substituents, whereas in the other substituents the HOMO energy level electron densities are in quinoline and pyrazoline moiety. (b) While forming cation radical of PAQ-NET<sub>2</sub> the charge of diethylamino group nitrogen is much lowered, whereas the other substituent cation radical shows the charge reduction mainly at one of the nitrogen in pyrazoline moiety.

(20) It is also noted that the strong electron-donating substituent, methoxy group, did not shift the PL spectra to further blue, which may be due to the involvement of lone pair electrons on oxygen, leading to different characteristic (similar to PAQ-NET<sub>2</sub>).

(21) Matsumara, M.; Akai, T. *Jpn. J. Appl. Phys., Part 1* **1996**, *35*, 5357.

(22) Jones-II G.; William, W. R.; Jackson, R.; Choi, C. Y. Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.

(23) Zhilin, Z.; Xueyin, J.; Shaohong, X. *Thin Solid Films* **2000**, *363*, 61.

Table 2. Performance of PAQ-Based LEDs

|                      | turn-on voltage (V) | voltage <sup>a</sup> (V) | brightness <sup>a</sup> (Cd/m <sup>2</sup> ) | ex quantum efficiency <sup>a</sup> (%) | power efficiency <sup>a</sup> (lm/W) | CIE coord <i>x</i> , <i>y</i> |
|----------------------|---------------------|--------------------------|--|--|--------------------------------------|-------------------------------|
| PAQ-OMe              | 4.5                 | 7.4                      | 584  | 2.93                                   | 1.03                                 | 0.16, 0.11                    |
| PAQ- <i>t</i> -Bu    | 4.5                 | 7.3                      | 570  | 3.00                                   | 1.00                                 | 0.16, 0.09                    |
| PAQ-H                | 5.0                 | 8.6                      | 522  | 2.46                                   | 0.78                                 | 0.16, 0.10                    |
| PAQ-F                | 5.3                 | 9.3                      | 538  | 2.03                                   | 0.71                                 | 0.17, 0.13                    |
| PAQ-CF <sub>3</sub>  | 6.4                 | 9.4                      | 158  | 0.49                                   | 0.21                                 | 0.16, 0.16                    |
| PAQ-CN               | 5.5                 | 9.4                      | 450  | 1.53                                   | 0.60                                 | 0.16, 0.15                    |
| PAQ-NET <sub>2</sub> | 4.1                 | 6.8                      | 1169   | 2.12                                   | 2.15                                 | 0.21, 0.38                    |

<sup>a</sup> Measured at 25 mA/cm<sup>2</sup>.

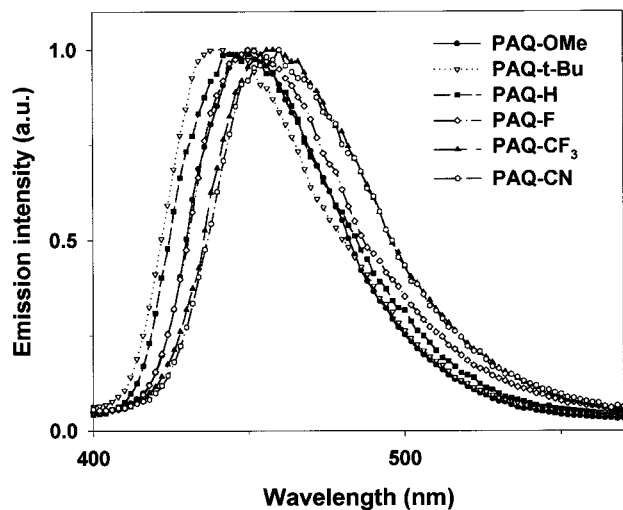


Figure 3. Normalized EL spectra of ITO/NPB/CBP/TPBI:PAQ/TPBI/Mg:Ag devices, where PAQ concentration were around 2%.

be discussed later. As a consequence of the small shift among different substitution, the Commission Internationale de L'Eclairage (CIE) coordinates are varying, and the values are shown in Table 2. A comparison of the EL spectra and CIE values as well as PL spectra of the PAQ materials unambiguously leads to the conclusion that the emission comes from the dopant. The TPBI is a good host material, and an efficient energy transfer can be obtained from TPBI to PAQ. The current–voltage–luminescence characteristics of ITO/NPB/CBP/TPBI:PAQ-X/TPBI/Mg:Ag devices are shown in Figure 4. The maximum brightness for the blue emission ranges between 5000 and 6000 cd/m<sup>2</sup> for various substituted PAQ. The device performances are dependent on substitution, and the data are compared in Table 2. The turn-on voltage and electrical property (voltage for obtaining a constant current) are also varying with substituents, i.e., lower for PAQs with electron-donating substituents such as MeO and *t*-Bu groups (<7.5 V) and higher for electron-withdrawing substituents such as CF<sub>3</sub> and CN groups (>9.3 V). Importantly, the device efficiency (external quantum efficiency and power efficiency) shows a similar substituent effect: more efficient for PAQs with electron-donating groups and less efficient for PAQs carrying an electron-withdrawing group.<sup>24</sup> It is also noted that the external quantum efficiency for the same PAQ-based devices increased 5.2

(24) Although the CN group is generally considered more electron-withdrawing than the CF<sub>3</sub> group, molecular modeling (with Spartan program of Wavefunction, Inc.) showed that the PAQ-CF<sub>3</sub> has a higher dipole moment (3.82 D) than PAQ-CN (2.76 D). The oxidation potential also implied that PAQ-CF<sub>3</sub> is slightly more electron-deficient.

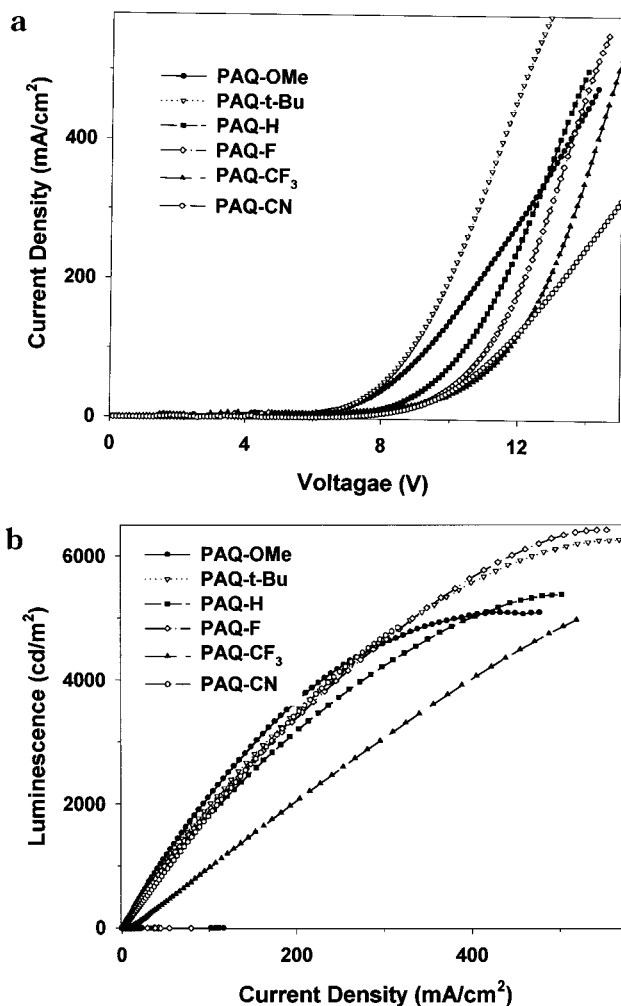


Figure 4. (a) Current–voltage characteristics and (b) current–luminescence characteristics of ITO/NPB/CBP/TPBI:PAQ/TPBI/Mg:Ag devices, where PAQ concentration were around 2%.

times as compared to our initial experiments using PBD (2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole) as the electron-transporting material.<sup>25</sup>

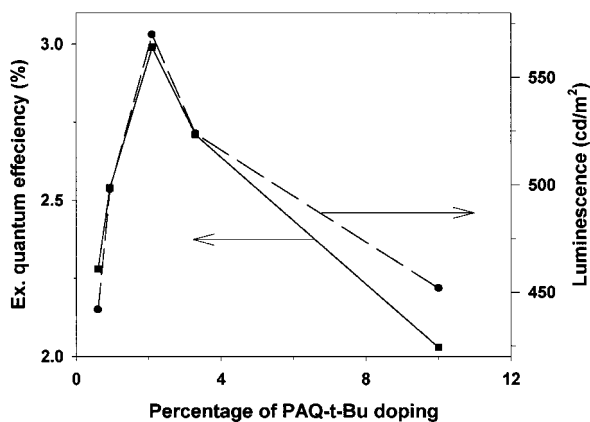
To understand the better performance of devices with PAQ carrying electron-donating substituents, we further estimated the relative energy levels using cyclic voltammetry and absorption spectra.<sup>12a,26</sup> The relative HOMO–LUMO energy levels data are summarized in Table 3. As expected, with strong electron-withdrawing

(25) Tao, Y. T.; Balasubramaniam, E.; Tomasik, P.; Danel, A.; Jarosz, B. The Proceeding for 8th Asian Chemical Congress, Taipei, 1999; p 336.

(26) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.

Table 3. Energy Alignment in PAQ Dyes

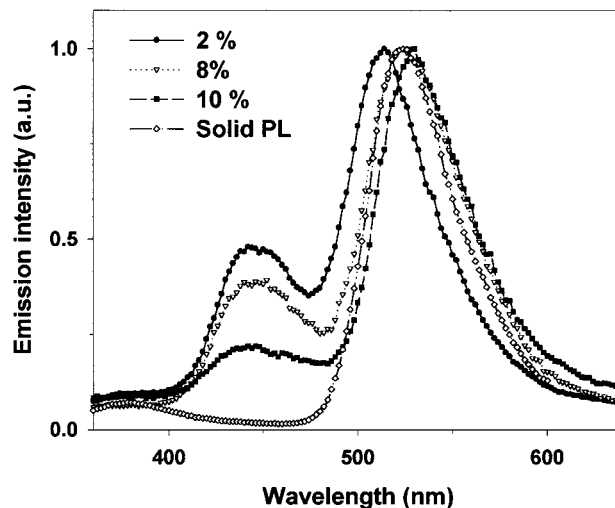
|                      | $E_{ox}$ , V | HOMO, eV       | band gap, eV | LUMO, eV       |
|----------------------|--------------|----------------|--------------|----------------|
| PAQ-OMe              | 1.37         | 5.77           | 2.77         | 3.00           |
| PAQ- <i>t</i> Bu     | 1.46         | 5.86           | 2.91         | 2.95           |
| PAQ-H                | 1.59         | 5.99           | 2.86         | 3.13           |
| PAQ-F                | 1.63         | 6.03           | 2.87         | 3.16           |
| PAQ-CF <sub>3</sub>  | 1.73         | 6.13           | 2.80         | 3.33           |
| PAQ-CN               | 1.69         | 6.09           | 2.75         | 3.34           |
| PAQ-NEt <sub>2</sub> | 0.74         | 5.14           | 2.51         | 2.63           |
| ITO                  |              | 4.70 ( $E_F$ ) |              |                |
| NPB                  | 0.83         | 5.23           | 3.03         | 2.20           |
| CBP                  |              | 5.50           |              | 2.00           |
| TPBI                 | 1.80         | 6.20           | 3.50         | 2.70           |
| Mg:Ag                |              |                |              | 3.70 ( $E_F$ ) |



**Figure 5.** Plot of device performance vs concentration of PAQ-*t*-Bu in the device configuration ITO/NPB/CBP/TPBI:PAQ/TPBI/Mg:Ag.

or weak electron-donating substituent groups, the removal of electron gets harder and the oxidation potential is raised and the HOMO energy level is lowered. In particular, the oxidation potential of PAQ-NEt<sub>2</sub> is much lower, which may be due to the involvement of lone pair electrons on the nitrogen atom.<sup>19</sup> In OLEDs, it is noted that the relative HOMO–LUMO energy levels of dopant (PAQ materials) are well within that of the host material (TPBI). Therefore, the emission from PAQ materials may happen either by energy transfer mechanism or by carrier trapping mechanism and which could be differentiated by a concentration-dependent study.<sup>27</sup> The concentration dependence studies are carried out for the strong electron-withdrawing substituent (PAQ-CF<sub>3</sub>) and the electron-donating substituent (PAQ-*t*-Bu). The similar spectral pattern in EL and in solid PL for both cases suggests that the energy transfer to be the major mechanism for the emission. However, on the basis of the quantum yields of the various PAQ dyes, one would expect a better device performance from PAQ-CF<sub>3</sub> by an energy transfer mechanism. But the poor device performance for PAQ with electron-donating substituent are attributed to the different energy transfer efficiency. The concentration dependence study for PAQ-*t*-Bu in TPBI also suggested a stable performance of the devices, as shown at Figure 5. It could be noted that the external quantum efficiency/luminescence drop in going from 2% to 10% dopant concentration. This may be due to self-quenching of the dopant emission at higher concentration. But the efficiency remains more than 2%, and luminescence

(27) Uchida, M.; Adachi, C.; Koyama, T.; Taniguchi, Y. *J. Appl. Phys.* **1999**, *86*, 1680.



**Figure 6.** PL spectra of TPBI:2% (w/w) PAQ ( $\lambda_{ex} = 302$  nm) and normalized EL spectra of ITO/NPB/CBP/TPBI:PAQ/TPBI/Mg:Ag devices, where PAQ is PAQ-NEt<sub>2</sub>.

change is within 10%. This is a useful parameter because of practical difficulty to maintain an exact doping concentration by coevaporation.

Along with the blue-emitting PAQ materials, a green-emitting PAQ-NEt<sub>2</sub> is also used as dopant in ITO/NPB/CBP/TPBI:PAQ/TPBI/Mg:Ag configuration. The EL is blue-green, and spectra are shown in Figure 6. It is to be mentioned that the spectral overlap between emission spectrum of TPBI and absorption spectra of PAQ-NEt<sub>2</sub> is poor. Also, the HOMO–LUMO energy levels of PAQ-NEt<sub>2</sub> are not within the energy levels of TPBI. (The LUMO is slightly higher than that of TPBI.) Thus, the PAQ-NEt<sub>2</sub> is a rare choice for doping in TPBI. However, Figure 6 suggests that the PAQ-NEt<sub>2</sub> material can be used for blue-green emission. The concentration of PAQ-NEt<sub>2</sub> in TPBI is varied from 2 to 10%. In all cases the EL is obtained with two emission peaks, i.e., with 450 and 520 nm peaks. But the intensity of the 520 nm peak is increasing with increasing concentration of PAQ-NEt<sub>2</sub>. This implies that there is an energy transfer from TPBI to PAQ-NEt<sub>2</sub>, given the low spectral overlap (~10%). The EL peak around 450 nm is not due a residual emission of TPBI as the solid PL spectrum of a TPBI film doped with 2% PAQ-NEt<sub>2</sub> shows a remaining TPBI emission at around 375 nm (Figure 6). The blue emission in the EL may be due to emission from NPB and/or CBP, which are known to emit in this region.<sup>28</sup> Nevertheless, the device performances of 2% (w/w) PAQ-NEt<sub>2</sub> doped ITO/NPB/CBP/TPBI:PAQ/TPBI/Mg:Ag are still significant, if not as good as the one doped in hole-transporting NPB.<sup>13</sup> The peak luminescence for blue-green emission is 14 000 cd/m<sup>2</sup> at 15 V. The external quantum efficiency and luminescence efficiency are also high (Table 2). It should be noted that the apparently better efficiency for the green PAQ-NEt<sub>2</sub>-based device is due to the sensitivity of human eyes in the green region.<sup>29</sup>

(28) A reference ITO/NPB/CBP/TPBI/Mg:Ag device was constructed and shows an EL with contribution from all three organic layers. This implies that (a) the excitons appear in all three regions or (b) the radiative energy transfer from TPBI to NPB and/or to CBP is occurring when the light was emitted through this media.

(29) Roberts, D. A. *Photonics Spectra* **1987**, 59.

In conclusion, we have prepared and used several new pyrazoloquinoline derivatives in fabricating organic light-emitting diodes. With TPBI as the host, these PAQ materials are emitters for blue and green emission. The efficiency and performance of the devices show dependence on the substituent, better for electron-donating groups and poorer for electron-withdrawing groups. The external quantum efficiency of the devices reach as high as 3.0% for electron-rich PAQ (PAQ-*t*-Bu, PAQ-OMe) doped devices, and the efficiency is not altered much for marginal error in doping.

**Acknowledgment.** We thank Academia Sinica, China Petroleum Corporation (Grant NSC 89-CPC-7-001-003), and Polish Scientific Committee (Grant 8 T11B 075 18) for their financial support.

**Supporting Information Available:** Synthesis of variously substituted pyrazoloquinolines as emitting material (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM000622J