MATERIALS CHEMISTRY COMMUNICATION

Blue electroluminescence of novel pyrazoloquinoline and bispyrazolopyridine derivatives in doped polymer matrices

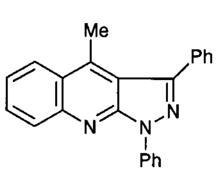
Z. He,[a†] G. H. W. Milburn,[a] A. Danel,[b] A. Puchala,[c] P. Tomasik[b] and D. Rasala[c]

[a] *ACPS, Napier University, Edinburgh, EH10 5DT, UK*
[b] *Department of Chemistry, University of Agriculture, 31 129 Cracow, Poland*
[c] *Institute of Chemistry, Pedagogical University, Kielce, Poland*

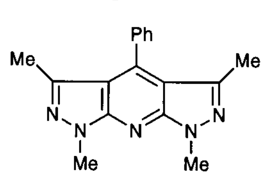
Blue electroluminescence has been demonstrated using novel materials 1,3-diphenyl-4-methyl-1*H*-pyrazolo[3,4-*b*]quinoline (PAQ4) and 4-phenyl-1,3,5,7-tetramethyl-1,7-dihydrodipyrazolo[3,4-*b*;4′,3′-*e*]pyridine (PAP1) for the first time. The peak maxima of their electroluminescent spectra were at 442 nm (*ca.* 20 nm shift from its photoluminescent maximum) for PAQ4 and 425 nm (within the same spectral range as the photoluminescence) for PAP1.

Electroluminescent (EL) devices based on organic or polymeric materials have received considerable attention in recent years since the successes reported by Tang[1] and by the Cambridge group.[2] The advantages that have been reported in using organic materials to fabricate electroluminescent devices are their high brightness, high efficiency and potential colour tuning, as well as their low cost of fabrication.[1–5] These new technologies have shown great commercial potential. For device applications, blue is one of the principal colours used in order to achieve a white emission in combination with others. However, the common characteristics of blue emitters are their large optical band gaps, as these are required in order to achieve an emission at relatively high energy. This may consequently restrict the injection characteristics and the conductivity as a result of limited delocalisation. This subject has attracted much attention in the search to develop novel blue emitting materials and the study of their electroluminescence properties.

In this communication, the electroluminescence characteristics of novel materials, 1,3-diphenyl-4-methyl-1*H*-pyrazolo[3,4-*b*]quinoline (PAQ4) and 4-phenyl-1,3,5,7-tetramethyl-1,7-dihydrodipyrazolo[3,4-*b*;4′,3′-*e*]pyridine (PAP1) are described for the first time. The materials were selected from a series of novel pyrazoloquinoline and dipyrazolopyridine derivatives which showed blue fluorescent spectra.



PAQ4



PAP1

The preparation of the materials[6] and the study of the optical and fluorescent properties of the whole series[7] will be reported elsewhere. A brief description of these materials is included in the Appendix. The electroluminescent spectrum from a PAQ4 doped polymer matrix was centred at 442 nm, a 20 nm shift to blue in comparison with its photoluminescence, while the electroluminescence spectrum for a PAP1 doped matrix falls in the same spectral range as its photoluminescence, centred at 425 nm. The devices constructed in this study have not been optimised. Full characterisation of the material properties and optimisation of the device performances are currently on-going.

Results and Discussion

Optical absorption and photoluminescent (PL) spectra were obtained using a Hewlett Packard 8452A diode array spectrophotometer and a Perkin-Elmer LS-50B fluorescent spectrometer, respectively. Both PAQ4 and PAP1 emit in the blue spectral region and gave peak maxima in chloroform solution at 451 and 427 nm, respectively. The photoluminescent quantum efficiencies in solution were measured using a relative method with quinine sulfate and 9,10-diphenylanthracene as standards.[8] The resultant quantum efficiencies measured in chloroform were *ca.* 1 for PAQ4 and 0.8 for PAP1. The solid state photoluminescent spectra were measured from doped polymer films that were a few micrometers in thickness. The polymer host used in this case was poly(*N*-vinylcarbazole) (PVK). The solid state photoluminescence of the PAQ4 doped polymer matrix was found to be dependent on the dopant concentration. It was found that the photoluminescence of this matrix came solely from the deactivation process in PAQ4 when the dopant concentration is above 10 wt%.[7] About 1–10 wt% blue emitting material, PAQ4 or PAP1, was doped into the polymer and these doped matrices were used in the device fabrication in this study. The photoluminescence from either the PAQ4 or PAP1 doped PVK matrices shows a structureless peak with peak maxima centred at 464 and 430 nm, respectively (Fig. 1).

The electroluminescence characteristics were measured from a single-layered sandwich structure, which consisted of a thin layer of doped polymer film on top of an indium-tin-oxide (ITO) (Balzers) glass plate, and an aluminium top electrode.

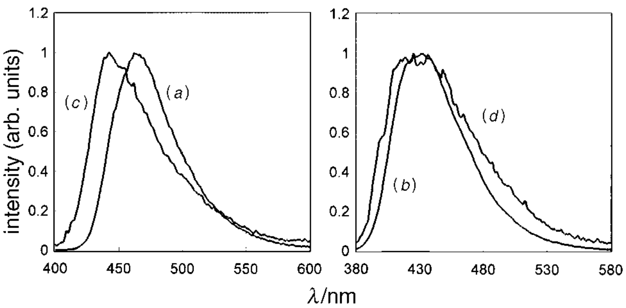


Fig. 1 PL emission spectra from (*a*) PAQ4 doped PVK and (*b*) PAP1 doped PVK, and EL spectra from (*c*) PAQ4 doped PVK and (*d*) PAP1 doped PVK

---

† E-mail: Z.He@napier.ac.uk

The ITO glass plate has a sheet resistance of 30 ohm sq^{-1}. The thin polymer film was spin-coated from a chloroform solution onto the ITO glass with a thickness of *ca.* 100 nm. The surface profile was monitored using a Talysurf machine. On top of the polymer layer, an aluminium electrode was vacuum evaporated at a pressure of $<8\times10^{-6}$ mbar and had a final thickness of 200 nm. Large emitting areas in the range of 10–20 mm^2 were used in the study.

Current, voltage and relative light intensity were measured using a Keithley 236 source measure unit combined with an amplified silicon photodiode and a digital multimeter. The measurements of current, voltage and light were performed simultaneously and fully controlled through a computer. The light detection was carried out by placing the photodetector as close as possible to the top of the electroluminescent electrode. Forward voltage or current pulses with a 100 ms 'on' time and a 500 ms 'off' time were used unless otherwise specified. Fig. 2 shows an example of the current–voltage and light–voltage characteristics from the PAQ4 device, in which the light output is almost linear in relation to the current density. The corresponding electroluminescent spectra were taken using a constant dc current drive. The device structure has not been optimised and the accurate efficiency measurement of these devices has not yet been carried out. An estimation of device efficiency for these initial devices was made according to the responsivity of the photodetector, which has an external quantum efficiency at a level of 0.1%.

Interesting results were obtained from a comparison of the electroluminescent spectra and the photoluminescent spectra (Fig. 1). It was found that the emission peak maximum of the electroluminescence from the PAQ4 device is shifted *ca.* 20 nm to the blue in comparison with its photoluminescence, while the electroluminescence spectrum fell within the same spectral range as the photoluminescent spectrum for the PAP1 device. This implies that the EL and PL may originate from a different recombination process in the PAQ4 device and from the same recombination process in the PAP1 device.

The mechanism of the operation of an organic electroluminescent device is not always straightforward. It is even more complicated in a multiple component system, such as polymer blends or polymers doped with one or more low molecular weight dyes. In these systems, the interaction between the different components cannot be ignored. Exciplex formation and energy transfer are also involved. Some typical devices have been reported. For example, exciplex formation is the principal electroluminescence obtained from 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene with an aromatic amine in a multilayer type device[9] and energy transfer is the principal electroluminescence in a 1,1,4,4-tetraphenylbuta-1,3-diene doped PVK multilayer device.[10] However, up to the present time, the type of emission produced by an electroluminescent device has not been predictable. Apart from the nature of each of the materials, the interaction between the different components can play an important role as well.

In our further investigation of the photoluminescent properties of the PAQ4 doped PVK matrices, we found that the interaction between PVK and PAQ4 is strong. PAQ4 was able to quench PVK photoluminescence effectively and transfer energy from PVK to PAQ4. From Fig. 3, it can be seen that PVK photoluminescence was completely quenched at a concentration of about 10 wt% of PAQ4 dopant. At the same time, the photoluminescent emission wavelengths from PAQ4 shifted continuously from 438 to 464 nm as the concentration increased from 10^{-5} to 12 wt% (Fig. 3). These results suggest that at low concentration, PAQ4 and PVK interaction was dominant. The photoluminescence of PAQ4 was maintained around 440 nm. At higher concentration, dopant–dopant interaction may occur. The emission wavelength shifted significantly as the dopant concentration increased. In the comparison of the two curves in Fig. 3, it was realised that the photoluminescent intensities from PVK started to decrease around the concentration level at which the dopant–dopant interaction occurred. Therefore, the energy transfer which occurred in the photoluminescence from this doped matrix was a process of the transfer of the excitation energy in PVK to the new species formed through the dopant–dopant interaction, but not to that species formed through the dopant–polymer interaction.

In the electroluminescence case, the 442 nm centred emission for the PAQ4 device implies a difference between the photoluminescent and electroluminescent excitation mechanisms. However, it is reasonable to suggest that this emission centre may be dominated by the species formed through the PAQ4 and PVK interaction, *i.e.* the dopant–polymer interaction, rather than the dopant–dopant interaction. The explanation of why this happens in PAQ4, but not in PAP1, is not yet known. This will be the subject of our further investigations of these materials.

Summary

We have demonstrated blue electroluminescence from the novel materials 1,3-diphenyl-4-methylpyrazolo[3,4-*b*]quinoline (PAQ4) and 4-phenyl-1,3,5,7-tetramethyl-1,7-dihydrodipyrazolo-[3,4-*b*; 4′,3′-*e*]pyridine (PAP1). These materials have been incorporated into a simple device: a single layer consisting of a poly(*N*-vinylcarbazole) host, which was previously doped with either PAQ4 or PAP1. ITO and aluminium were used as hole and electron injection electrodes, respectively. The electroluminescent spectra were found to have an emission maximum in the blue spectral range, with a peak wavelength of 442 nm (showing a 20 nm shift from the photoluminescent spectrum)

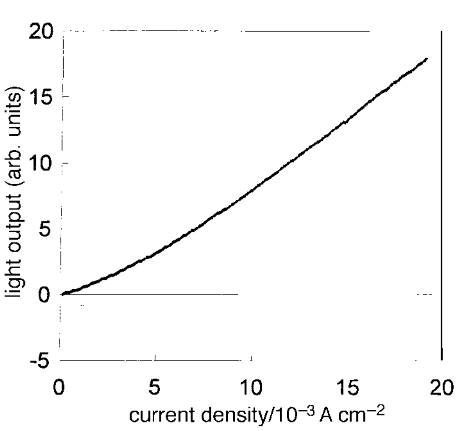


Fig. 2 Light and current density dependence from an EL device consisting of PAQ4 doped PVK layer

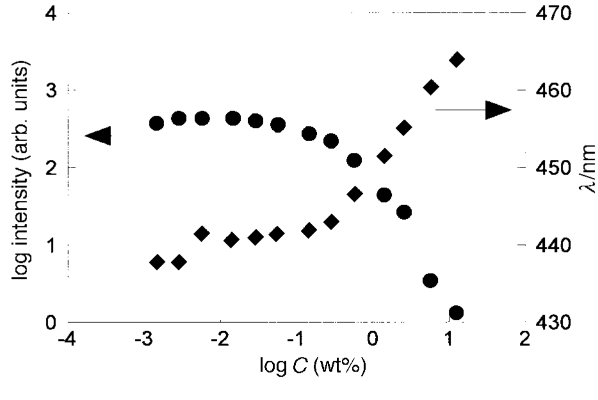


Fig. 3 A comparison of (◆) the concentration dependence of PL emission wavelength at maximum peak intensity from PAQ4 and (●) PVK PL intensities as a function of the PAQ4 concentration of the PAQ4 doped PVK matrices

for PAQ4, and 425 nm (within the same spectral range as the photoluminescence) for PAP1. The shift of the electroluminescent peak in the PAQ4 device is explained by the domination of the dopant–polymer interaction. Further investigation of the material property evaluation and optimisation of device performance are still in progress.

Appendix

1,3-Diphenyl-4-methylpyrazolo[3,4-*b*]quinoline (PAQ4)

A mixture of equimolar amounts (0.01 M) of 1,3-diphenylpyrazolin-5-one and 2-aminoacetophenone was heated at 180 °C in ethylene glycol (5 ml) for 24 h. After the mixture was cooled, EtOH was added. The crystalline precipitate was filtered and then washed with EtOH and recrystallised from toluene. Yellow crystals were obtained (Yield, 63%); mp 174–175 °C (Calc. for $C_{23}H_{17}N_3$: C, 82.37; H, 5.11; N, 12.52. Found: C, 82.28; H, 4.98; N, 12.48%); δ_H ($CDCl_3$) 2.78(s, 3H), 7.29(t, 1H), 7.44(t, 1H), 7.50–7.56(m, 5H), 7.71–7.47(m, 3H), 8.11(d, *J* 8.26 Hz, 1H), 8.14(d, *J* 8.62 Hz, 1H), 8.56(d, *J* 7.59 Hz, 2H); δ_C ($CDCl_3$) 15.48, 116.32, 120.73, 123.81, 124.36, 125.22, 128.35, 128.94, 129.47, 130.06, 130.24, 133.96, 139.89, 141.36, 146.81, 148.05, 150.03.

4-Phenyl-1,3,5,7-tetramethyl-1,7-dihydrodipyrazolo-[3,4-*b*;4′,3′-*e*]pyridine (PAP1)

A mixture of 5-amino-1,3-dimethylpyrazole (0.05 mol) and benzaldehyde (0.025 mol) was heated at 120–140 °C. After *ca.* 30 min, gas evolution had ceased and the reaction was allowed to continue for an additional 3 h at 240 °C. It was then cooled to room temperature, and the resulting solid was recrystallised from ethanol–water (4 : 1) to give 2.3 g (42%) of 4-phenyl-1,3,5,7-tetramethyl-1,7-dihydrodipyrazolo[3,4-*b*;4′,3′-*e*]pyridine (mp 164–165.5 °C). The sample was further purified by column chromatography on Merck silica gel using CH_2Cl_2 as eluent. The purified sample had a melting temperature of 165–166 °C (Calc. for $C_{17}H_{17}N_5$: C, 70.07; H, 5.90; N, 24.03. Found: C, 70.25; H, 6.01; N, 24.12%); δ_H ($CDCl_3$) 7.49–7.52(m, 3H), 7.38–7.39(m, 2H), 4.06(s, 3H), 2.00(s, 3H); δ_C ($CDCl_3$) 151.71, 141.88, 140.77, 134.62, 128.61, 128.53, 127.69, 111.20, 33.17, 14.52.

References

1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
2. J. H. Burroughs, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
3. C. W. Tang, S. A. VanSlyke and C. H. Chen, *J. Appl. Phys.*, 1989, **65**, 3610.
4. Y. Ohmori, M. Uchida, K. Muro and K. Yoshino, *Jpn. J. Appl. Phys.*, 1991, **30**, L1941.
5. J. Kido, K. Honggawa, K. Okuyama and K. Nagai, *Appl. Phys. Lett.*, 1993, **63**, 2627.
6. A. Danel, K. Danel, P. Tomasik and G. H. W. Milburn, unpublished work.
7. Z. He, G. H. W. Milburn, K. J. Baldwin, D. A. Smith, A. Danel and P. Tomasik, unpublished work.
8. J. V. Morris, M. A. Mahaney and J. R. Huber, *J. Phys. Chem.*, 1976, **80**, 969
9. C. Adachi, T. Tsutsui and S. Saito., *Appl. Phys. Lett.*, 1990, **56**, 799.
10. J. Kido, K. Hongawa, K. Okuyama and K. Nagai, *Appl. Phys. Lett.*, 1994, **64**, 815.

Communication 7/06561B; *Received* 8*th September*, 1997