Macromol. Symp. **2004**, *212,* 473-478

Pyrazoloquinolines – Alternative Chromophores for Organic LED Fabrication

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Summary: In this paper the synthesis of some new chromophores which could be used in polymer/organic LED fabrication are presented. All of them are pyrazoloquinoline (PAQ) derivatives. Their emission properties were tuned by side group substitution. They were characterized by absorption and photoemission spectroscopy. Some were used, dispersed in poly(*N*-vinylcarbazole) (PVK) matrix, as the emissive layer in LED structures.

Keywords: dyes; electroluminescence; fluorescence; light emitting diodes (LED); pyrazoloquinolines

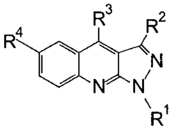
Introduction

Polymer and/or organic light-emitting diodes (LEDs) have the potential to radically change the display technology by enabling cheap, colour and flat displays with viewing properties similar to traditional cathode ray tubes. Other interesting applications like large surface lighting or back-lighting are also possible. Although organic and/or polymer LEDs have been the subject of extensive research since the beginning of the nineties and many compounds emitting in the green region are already known, there is still important demand for materials having their intense emission in the blue and red regions to produce full-colour RGB displays. In this paper new 1*H*-pyrazolo[3,4-*b*]quinoline (PAQ) derivatives with properties appropriate for these applications are reported. Such compounds exhibit strong fluorescence in solution [1-3] and also in the solid state [1] - a desirable property for high-performance electroluminescent devices. Recently, some other 1*H*-pyrazolo[3,4-*b*]quinoline derivatives have been used in light-emitting devices in the form of molecular layers [4,5].

DOI: 10.1002/masy.200450860

Synthesis

The general structure of synthesized PAQ derivatives is in Fig. 1.



Compound	R^1	R^2	R^3	R^4
PAQ1	Ph	Me	4-$MeOC_6H_4$	Me_3C
PAQ2	Ph	Me	4-$MeOC_6H_4$	F
PAQ3	Ph	Me	4-$MeOC_6H_4$	MeO
PAQ4	Ph	Me	Ph	-
PAQ5	Ph	Ph	Ph	-
PAQ6	Me	Me	Me	-
PAQ7	Me	Ph	Ph	-

Figure 1. General structure of 1*H*-pyrazolo[3,4-*b*]quinoline derivatives

Depending on the substituents, one of the three methods described below was used for the synthesis of a particular PAQ derivative. The most important synthetic method includes the Friedländer condensation of 1,3-disubstituted 4,5-dihydro-1*H*-pyrazol-5-ones with anthranilaldehyde (Fig. 2). The reaction is performed usually in the melt or in diethylene glycol. The other reactions include cyclisations of benzoic acid derivatives (Fig. 3). Since anthranilaldehydes and 2-aminobenzophenones and acetophenones are not readily available, the reaction of 5-chloro-4-formylpyrazoles or 4-aroyl-5-chloropyrazoles with substituted anilines [6] (Fig. 4) was used for the synthesis of 1*H*-pyrazolo[3,4-*b*]quinolines. Due to these reactions the modifications of the carbocyclic ring is very easy.

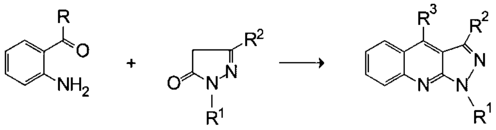


Figure 2. Friedländer condensation. R = H, Me, Ph ; R^1, R^2 = H, Me , Ph

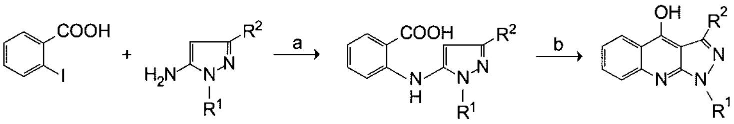


Figure 3. Cyclisations of benzoic acid derivatives a K_2CO_3 / CuO /H_2O; b polyphosphoric acid, 100 °C

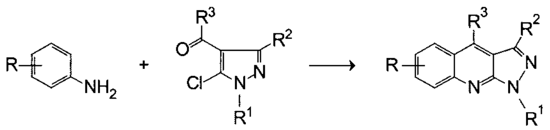


Figure 4. Reaction of 5-chloro-4-formylpyrazoles or 4-aroyl-5-chloropyrazoles with substituted anilines (R = H, MeO, NEt_2, Cl, Br; R^1, R^2 = Me, Ar; R^3 = H, Ar)

These methods suffer from certain limitations and disadvantages. Their application to the preparation of 4-aryl derivatives is restricted by the availability of 2-aminobenzophenones and aroylpyrazoles. Mostly, multistep syntheses are required for their preparation. Recently, an improved synthesis of 4-aryl-1*H*-pyrazolo[3,4-*b*]quinolines from aromatic amines and 4-benzylidene-4,5-dihydro-1*H*-pyrazol-5-ones [7] (Fig. 5), and also their one-pot synthesis [8] were described (Fig. 6). In the latter case it is very easy to modify aromatic ring in position 4 and to introduce the heterocycling ring.

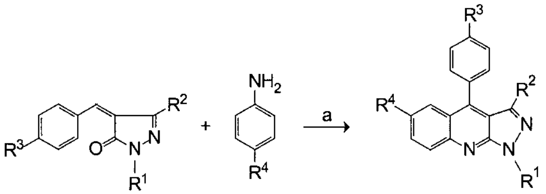


Figure 5. Improved synthesis of 4-aryl-1*H*-pyrazolo[3,4-*b*]quinolines (R = H, MeO, NEt_2, Cl, Br; R^1, R^2 = Me, Ar; R^3 = H, Ar) (under microwave irradiation)

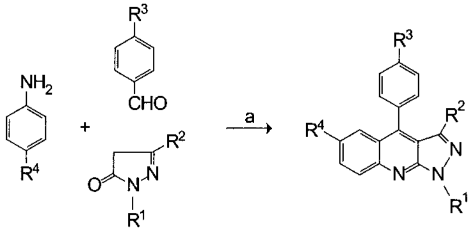


Figure 6. One-pot synthesis of 4-aryl-1*H*-pyrazolo[3,4-*b*]quinolines (in ethylene glycol, 190 °C, 1-2 h)

Experimental

Absorption and photoluminescence spectra of the synthesized compounds were measured in THF solution (Table 1). No simple correlation between positions of photoluminescence maxima and structures of the molecules was observed.

Table 1. Absorption (HOMO-LUMO transition), photoluminescence and electroluminescence maxima (nm).

Compound	Absorption	Photoluminescence	Electroluminescence
PAQ1	394	448	453
PAQ2	399	465	460
PAQ3	412	457	456
PAQ4	394	466	456
PAQ5	397	474	459
PAQ6	396	438	434
PAQ7	398	429	429

It was found in one of previous publications [1,4,5] that almost all PAQ derivatives rapidly crystallize from solutions when evaporated, which normally shifts electroluminescence spectra towards the red end of visible region. For this reason, the electroluminescence properties were measured in a simple sandwich structure ITO/PVK-PAQ/Ca/Al, where the active layer of PVK polymer was obtained from a solution of PVK and PAQ in THF by spin-casting. The most advantageous concentration of this dopant, at which the emitted light was of the highest intensity, was 1 wt. % As one can see in Table 1 and in Fig. 7, the maximum of electroluminescence spectra ranged between 430 and 460 nm. The shortest maxima wavelengths were observed for compounds PAQ6 and PAQ7. These spectra were less broad (ca. 50 nm) compared with the other (70 – 80 nm).

No effort was made to improve the geometry of the tested LEDs, because the main interest was to measure the electroluminescence spectra. Therefore the "turn-on" voltages were typically rather high, on average 12 V. Despite this inconvenience, it was still possible to estimate the relative quantum efficiency of the studied devices, because all of them had equal thickness. In Fig. 8, where luminescence/current dependences are shown, one can see that the strongest radiation combined with the least power consumption were found for LEDs with active layers doped with either PAQ4 or again PAQ7. In this last case, an estimate of the external quantum efficiency was ca. 1.5 %.

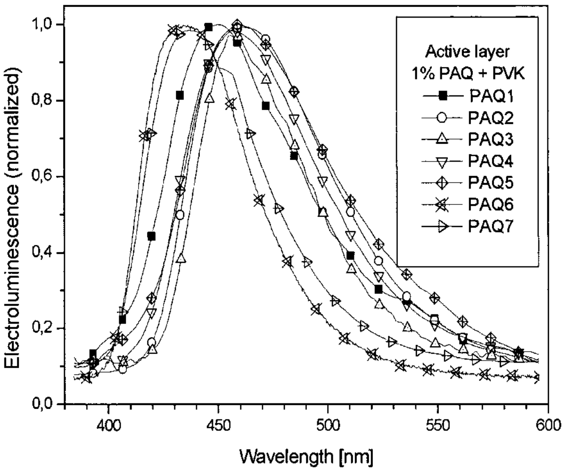


Figure 7. Normalized elektroluminescence spectra of LEDs with a PVK active layer doped with different pyrazoloquinolines

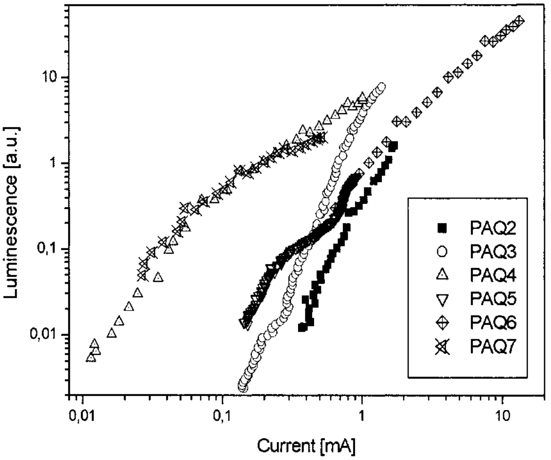


Figure 8. Luminescence of studied LEDs as a function of the flowing current

Conclusions

In this work seven new derivatives of 1*H*-pyrazolo[3,4-*b*]quinolines were synthesized and their photo- and electroluminescence properties were measured. 1-Methyl-3,4-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline was the most efficient dopant in the tested LEDs regarding its emission spectrum and quantum efficiency.

Acknowledgements

This work was partly supported through the KBN grant No. 8-T11-B-075-18. J. N. acknowledges the aid of the Marie Curie Fellowship Program No. HPMCFT-2000-00580.

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