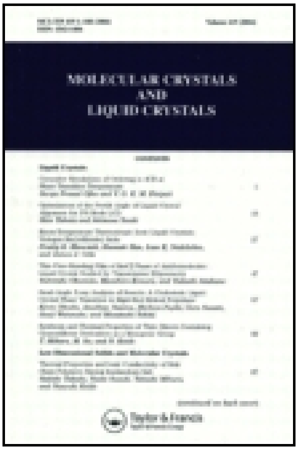

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Synthesis and Electro-Optic Properties of Pirazolo[3,4-b]Chinoline - PVK Copolymers

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Synthesis of new PVK and 1H-pyrazolo[3,4-b]quinoline based copolymers for electro-optic applications is described. Both copolymers are soluble and can be processed into thin films. A single layer OLED structure was fabricated and a blue light emission was observed. Although devices were not optimized, the "turn-on" bias voltage was relatively low, ca. 12 V.

Keywords: organic light emitting diode; PVK copolymers

INTRODUCTION

Chromophores from pyrazolo[3,4-b]chinoline family (PAQ) were extensively studied in recent years [1–4] owing to their good electro-optic properties and potential they present for applications in the fabrication

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of OLEDs. Typically, they were used in form of thin layer, obtained either by vacuum evaporation or by spin-coating, when blended with a host polymer. In both cases, like with many other molecular materials, their performances in OLED architectures were limited by chromophores aggregation. This phenomenon was also a source of accelerated device ageing and decreased its performances. In practice, chemical grafting of chromophore molecules on the polymer main chain helps to resolve these problems. In this article a new synthetic route to obtain copolymers of PAQ chromophores and vinyl-carbazole. These copolymers were characterized in the single layer OLED structure is described.

CHEMICAL SYNTHESIS

Schematic route of chromophore synthesis is shown in Figure 1. Two types of chromophores were synthesised, with substituents denoted in

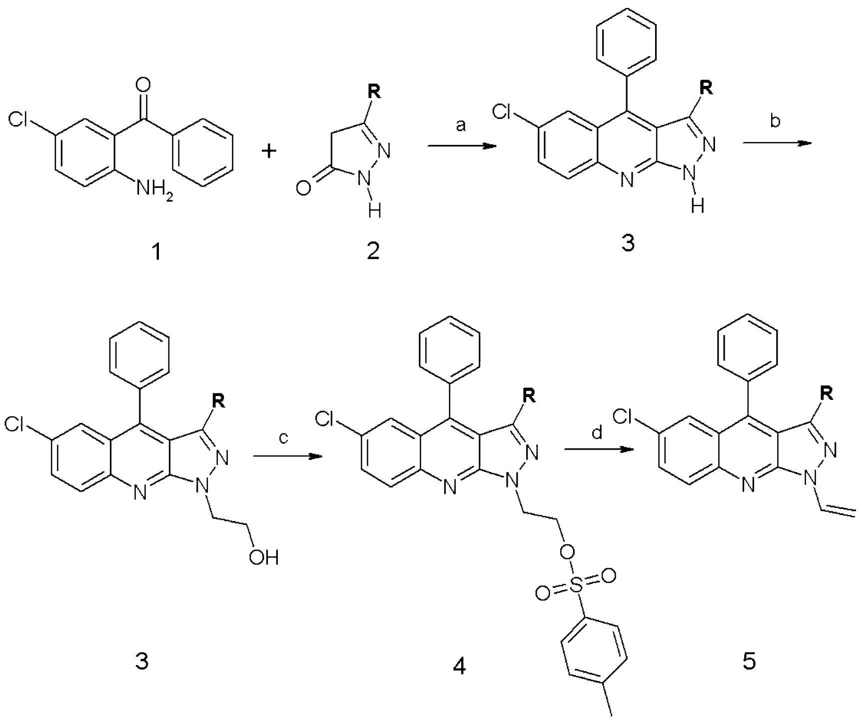

FIGURE 1 Scheme of synthesis of 1-vinyl-1*H*-pyrazolo[3,4-b]quinoline, (R = Ph, Me). Reaction conditions: (a) ethylene glycol, 190°C; (b) BrEtOH, K_2CO_3, DMF, 70°C; (c) p-TsCl, pyridine, 0°C; (d) t-BuOK, pyridine, 80°C.

Figure 1 as R being either Me or Ph group. Previous experience with these materials proved that such a difference in substitution could influence the solubility of the compound in common solvents. The subsequent stages of the synthesis are described below. If not specified explicitly, all chemicals were commercial products by Aldrich, used as received.

6-Chloro-3-methyl-4-phenyl-1*H*-pyrazolo[3,4-b]quinoline (Fig. 1 [3], R = Me)

5-Chloro-2-aminobenzophenone (6.95 g; 0.03 mol) and 5-methyl-2,4-dihydro-pyrazol-5-one were heated in diethylene glycol at 190°C for 24 h. After cooling the reaction mixture was digested with ethanol. After filtration the crude product was recrystallized from DMF and pale yellow crystals were obtained.

2-(6-Chloro-3-methyl-4-phenyl-1*H*-pyrazolo[3,4-b]quinolin-1-yl)-ethanol (Fig. 1 [4], R = Me)

Synthesised in the previous step 6-Chloro-3-methyl-4-phenyl-1*H*-pyrazolo[3,4-b]quinoline, bromoethanol and anhydrous potassium carbonate were heated together in anhydrous DMF for 24 h at 70°C. After this time the bromoethanol was added and heating was continued for the next 8 h at 70°C. Next, DMF was evaporated under reduced pressure and the oily residue was digested with water and acidified with 10% HCl. The precipitate was filtered off, dried and the product was purified by the column chromatography on alumina using toluene as eluent. Then the product was recrystallized from toluene/ethyl acetate/3:1 yielding yellow crystals.

Toluene-4-sulfonic acid 2-(6-chloro-3-methyl-4-phenyl-1*H*-pyrazolo[3,4-b]quinolin-1-yl)ethyl ester (Fig. 1 [5], R = Me)

To the obtained in previous stage 2-(6-Chloro-3-methyl-4-phenyl-1*H*-pyrazolo[3,4-b]quinolin-1-yl)-ethanol in pyridine at 0°C was added p-toluenesulfonyl chloride, also in pyridine, over 15 min. The reaction mixture was allowed to stand overnight at room temperature and then the solution was diluted with 10% HCl and extracted with chloroform. After drying (calcium chloride) the solvent was removed at reduced pressure and the product was purified by column chromatography on silica gel.

6-Chloro-3,4-diphenyl-1-vinyl-1*H*-pyrazolo[3,4-b]quinoline (Fig. 1[6], R = Me)

To the solution of toluene-4-sulfonic acid 2-(6-chloro-3-methyl-4-phenyl-1*H*-pyrazolo[3,4-b]quinolin-1-yl)ethyl ester (Fig. 1 [5], R = Me) in dry pyridine t-BuOK was added and heated at 80°C for 2 h. The cold mixture was acidified with 10% HCl. The crude product was dried and chromatographed over silica gel (Merck; silica gel 60) using chloroform/ethyl acetate 5:1 as eluent. The final product was in form of yellow crystals, mp. 171°C (toluene). It was identified by NMR and elemental analysis. The results were as follows:

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.15$ (d, $J = 9.0$ Hz, 1H); 7.96 (dd, $J = 15.7$ Hz; 9.1 Hz, 1H); 7.89 (d, $J = 1.9$ Hz, 1H); 7.73 (d, $J = 9.1$ Hz, 1H); 7.38 (t, $J = 7.3$ Hz, 1H); 7.32–7.06 (m, 9H); 6.08 (d, $J = 15.7$ Hz, 1H); 5.04 (d, $J = 9.1$ Hz, 1H). Calc. for $C_{24}H_{16}ClN_3$: C, 74.26; H, 3.97; N, 11.81. Found: C, 74.04; H, 3.78; N, 11.74.

PAQ molecule containing R = Ph, was synthesised in almost the same way, so the details are omitted here.

Polymerisation

Usually the content of PAQ chromophore in polymer matrix higher than 2% results in lowering of the emitted electroluminescence light intensity [5]. This limits the maximum content of PAQ groups in the synthesised copolymer. The applied procedure was as follows. In a three necked flask (50 ml) equipped with nitrogen inlet, reflux condenser, magnetic stirrer compound shown in Figure 1 [6] (R = Me Me or Ph) (0.1, 1 or 1.8 mol%), N-vinylcarbazole and 20 mg of AIBN

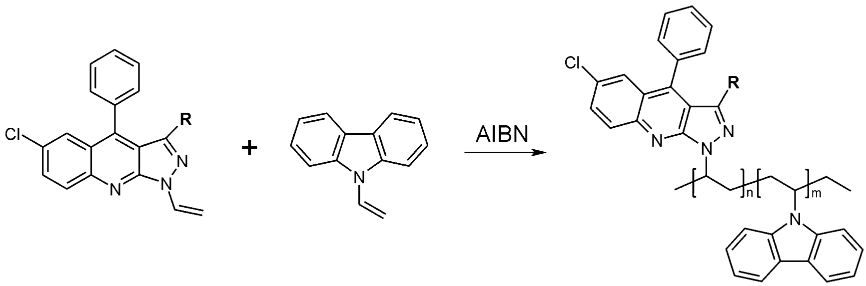

FIGURE 2 Copolymerization of pyrazolo[3,4-b]chinoline chromophore and N-vinylcarbazole. 'R' stands for either Ph or Me group. AIBN – azoizobutylonitrile in toluene.

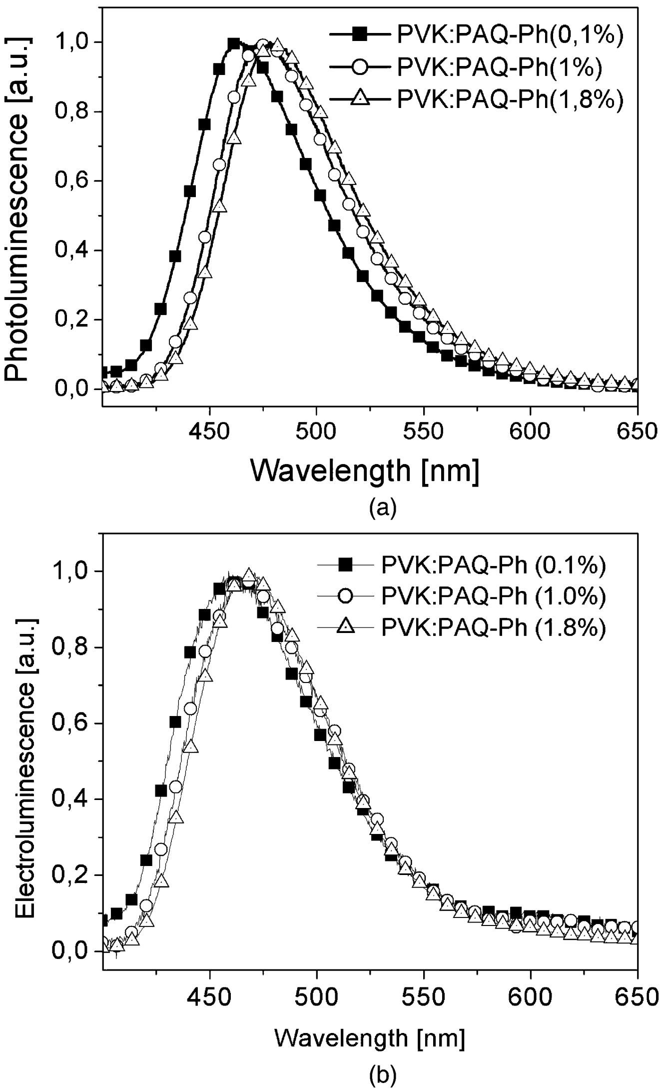

FIGURE 3 Comparison of (A) photo- and (B) electroluminescence of PVK: PAQ-Ph copolymers.

(azoizobutylonitrile) were dissolved in 50 ml of dry toluene (dried over sodium). A flow of nitrogen was maintained through the solution throughout the whole polymerization time (24 h). The reaction was carried at 70°C. The polymers were precipitated by pouring the reaction mixture into methanol (200 ml). After drying the solid was extracted in Soxhlet apparatus with methanol to remove unreacted starting materials and low-molecular weight oligomers. Schematic representation of this reaction is shown in Figure 2.

MEASUREMENTS

As already mentioned both copolymers were tested in sandwich OLED structure glass/ITO/polymer/Ca/Al. The films, ca. 100 nm thick, were obtained by the solution spinning technique. As it can be seen in Figure 3A and B the photo- and electroluminescence spectra of both copolymers are almost identical, with maximum emission wavelength around 465 nm. This wavelength correspond roughly to the blue colour. An increase of PAQ content from 0.1 to 1% results in a bathochromic shift of the emission spectra by about 10 nm when biased with more then the so-called turn-on voltage (defined in Fig. 4). The values of turn-on voltages for OLED made from copolymers and blends containing the same amount of chromophore were always lower in the case of copolymers. The obtained results are compared in Table 1.

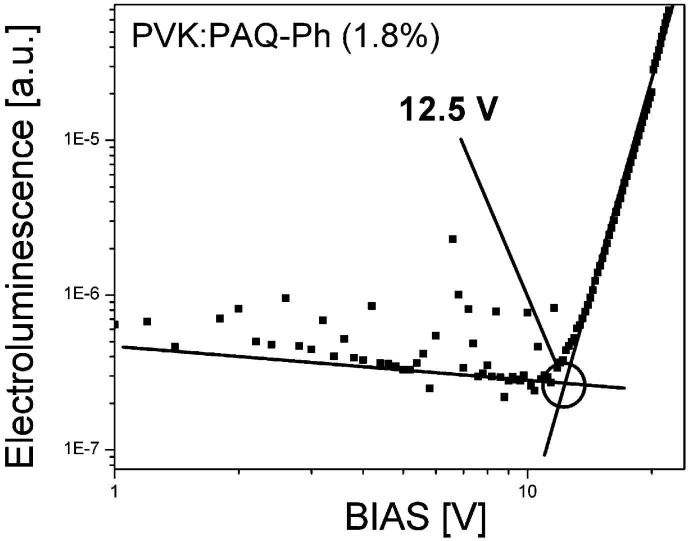

FIGURE 4 Electroluminescence intensity dependence on Bias voltage in case of PVK:PAQ-Ph (1.8%) containing OLED.

TABLE 1 Comparison of "Turn-on" Voltages for Copolymer and Blend based OLEDs with Different Chromophore Content

Composition of the active layer	Copolymer (V)	Blend (V)
PVK:PQ-Me (0,1%)	13,0	19,1
PVK:PQ-Me (1%)	15,1	18,2
PVK:PQ-Me (1,83%)	17,0	24,5
PVK:PQ-Ph (1,54%)	12,5	17,5

Usually, the OLEDs made from copolymers have also longer life span then their blend homologues.

In lower bias regime, when no light is emitted (until about 3 V) the charge transport can be understand in terms of the SCLC model [6] (straight line in Fig. 5). Above this value the tunelling processes cannot be neglected. The Fowler-Nordheim model [6] fits well experimental data in this region (almost up to the turn-on voltage).

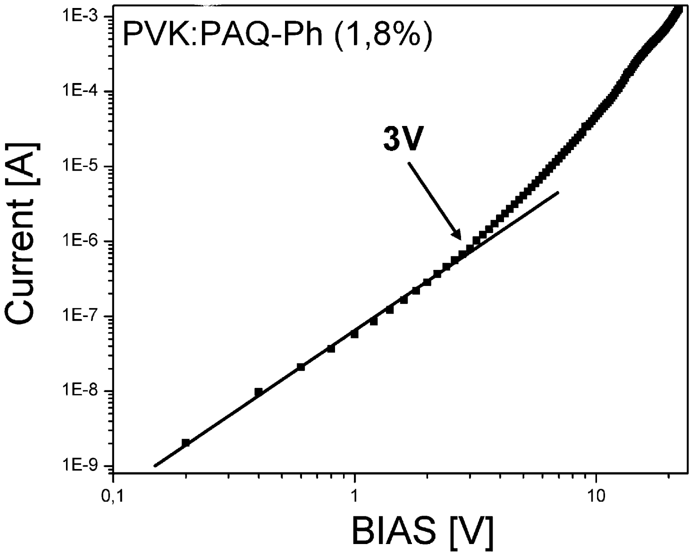

FIGURE 5 Bias-current characteristic of PVK:PAQ-Ph (1.8%) containing OLED, in non-emissive conditions. The intersection of two asymptotic lines to this characteristic defines turn-on voltage (at circled point).

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