EWA GONDEK[1], JERZY SANETRA[2], PAWEŁ ARMATYS[3], JACEK NIZIOŁ[3],
KAREN CHACZATRIAN[2], ANDRZEJ DANEL[2]

New pyrazoloquinolines and their application in organic light-emitting diodes with poly(*N*-vinylcarbazole) matrix

Summary — There were synthesized six new pyrazoloquinoline derivatives (PAQ) described with a formula (I), in which the meanings of R_4 substituent are as follows: -Br, -OC_6H_5, -CH_3, -H, -OCH_3, -Cl. The new compounds were characterized, among others, on the basis of ^{1}H NMR spectra and elemental analyses results. Mixtures of these PAQ derivatives with poly(N-vinylcarbazole) were applied in the organic light-emitting diodes (LED). Spectra of absorption, photoluminescence (PL) and electroluminescence (EL) of LEDs prepared were presented. It has been found that the type of R_4 substituent influences PL and EL quantum yields.

Key words: pyrazoloquinoline derivatives, poly(N-vinylcarbazole), organic light-emitting diodes, photoluminescence and electroluminescence.

Polymer and organic light-emitting diodes (LED) are believed to be an alternative to traditional cathode ray tubes in the applications which should combine cheap price and good imaging properties. The most important part of such kind of device is the emissive layer which is either polymer or low-molecular organic material (named as dye or chromophore) in their nature. Very often a combination of both is used in the form of a blend. Such organic LED always has a layered structure where the outermost layers are electrodes made of new conductive materials (the anode is usually transparent). The electroluminescence (EL) occurs when the positive and negative charge carriers are injected into a thin film of emissive layer, then form the exciton states which recombine emitting the light. The detailed description of physics associated with electroluminescence in polymer and organic materials can be found elsewhere [1, 2]. Although LEDs have been a subject of an extensive research since the beginning of the last decade [3], there is still important demand for materials showing an intense emission in the blue spectral region to produce full-colour flat displays. The derivatives of 1*H*-pyrazolo[3, 4-*b*] quinolines (PAQ) are potential candidates for the blue light electroluminescent materials [4—7] .

This work describes the synthesis and characterization of optical and electrooptical properties of a new series of PAQs derivatives. They differ in substitution of either electron-donating or electron-accepting side groups. The electrooptical properties of PAQ chromophores were tested in the blends with poly-*N*-vinylcarbazole (PVK) matrix. This matrix is transparent in the visible part of the light, represents good film-forming ability and high thermal stability. PVK itself is a very good holes conductor, but on the other hand its own blue EL quantum yield is far too low to meet application requirements. The addition of a suitable chromophore into PVK matrix improves EL properties and gives an opportunity to tune the colour of emitted light from violet to green. In the future some of chosen PAQ chromophores will be directly grafted onto PVK chain to obtain a pure polymer material which is easier to handling and transformation.

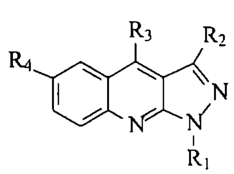
GENERAL CHARACTERISTIC OF 1*H*-PYRAZOLO [3, 4-*b*]QUINOLINES DERIVATIVES' PREPARATION

The most important synthetic method of 1*H*-pyrazolo[3, 4-*b*]quinolines derivatives [see Formula (I), further text] is Friedländer condensation of 2,5-disubstituted pyrazol-3-ones with anthranilic aldehyde [equation (1)]. The reaction usually is carried out in the melt or in diethylene glycol. Since anthranilic aldehydes and *o*-aminobenzophenones and acetophenones are not readily available, the reactions of 5-chloro-4-formylpyrazoles [8] or 4-aroyl-5-chloropyrazoles [9] with substituted anilines [equation (2)] were applied for the syntheses of PAQs derivatives. Due to these reactions the modifications of carbocyclic ring are very easy.

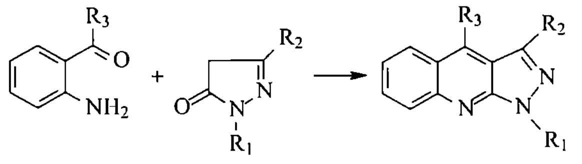
This method suffers certain limitations and disadvantages. Its application for preparation of 4-aryl derivatives is restricted by the availability of 2-amino-benzo-

---

[1] Cracow University of Technology, Institute of Physics, ul. Podchorążych 1, 30-084 Kraków, Poland.
[2] Hugon Kollataj Agricultural University, Departament of Chemistry, Al. Mickiewicza 24/28, 30-059 Kraków, Poland.
[3] University of Mining and Metallurgy, Faculty of Physics and Nuclear Techniques, Al. Mickiewicza 30, 30-059 Kraków, Poland.

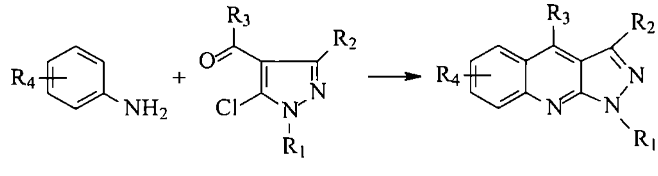


(I)



(1)

where: R_1, R_2, R_3 = H, Me or Ph

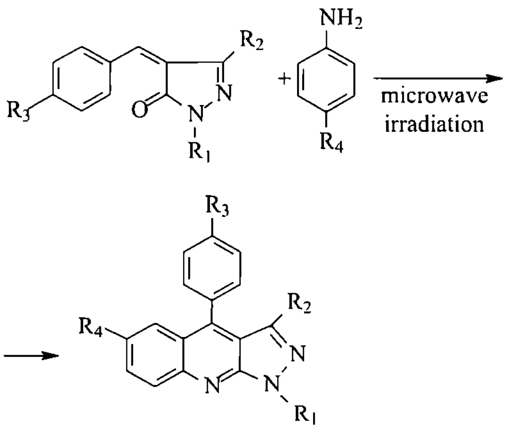


(2)

where: R_1, R_2 = Me, Ar; R_3 = H, Ar; R_4 = H, MeO, NEt_2, Cl, Br

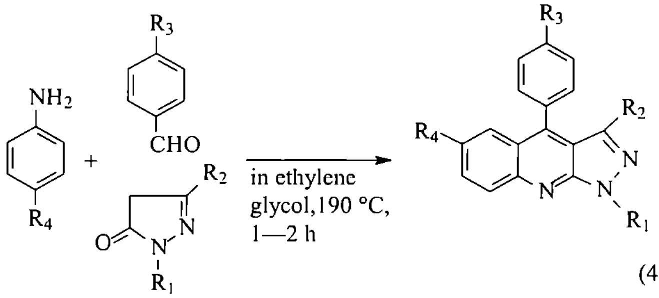
phenones and aroylpyrazoles. Usually a multi-step synthesis is required for the material preparation.

Recently, an improved synthesis of 4-aryl-1*H*-pyrazolo[3, 4-*b*]quinolines has become available from aromatic amines with 4-benzylidene pyrazolo-3-ones [10] [equation (3)]. Just recently one-pot synthesis (three-component reaction) of 4-aryl-1*H*-pyrazolo[3, 4-*b*]quinolines was developed in our home laboratory [11] [equation (4)]. It greatly facilitates the modification of the aromatic ring in the position 4 (with the introduction of heterocycling ring, too). The described routes were followed to synthesize of the chromophores being the subject of this work.



(3)

where: R_1, R_2 = Me, Ar; R_3 = H, Ar; R_4 = H, MeO, NEt_2, Cl, Br



(4)

EXPERIMENTAL

Synthesis of PAQs derivatives

Depending on the lateral group to be substitute, one of the three described below methods of a synthesis was used. The general structure of the synthesized PAQ's derivatives is shown in Formula (I). In the Formula (I) R_1 means phenyl group (Ph), R_2—methyl group (Me), R_3—*p*-tolyl group (*p*-CH_3-C_6H_4), while R_4 group has various meanings, as follows: -Br (sample PAQ1), -OC_6H_5 (PAQ2), -OCH_3 (PAQ3), -H (PAQ4), -CH_3 (PAQ5), -Cl (PAQ6).

The compounds PAQ4 and PAQ5 were prepared by condensation *p*-tolyl aldehyde with 5-(aryl)amino-3-methyl-1-phenylpyrazole in the presence of anhydrous zinc chloride according to Michaelis [4]. Compounds PAQ1, PAQ2, PAQ3, and PAQ6 were prepared by condensation of 3-methyl-1-phenyl-4-(*p*-methylphenylidene)pyrazolin-5-one with substituted anilines [equation (3)] using either conventional heating or microwave irradiation [10]. All of the compounds (except PAQ4) were also prepared paralelly by three component reaction [equation (4)] of aromatic aldehyde, amine and 3-methyl-1-phenylpyrazolin-5-one [11].

Characteristics of PAQs derivatives

4-(4′-Methylphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo [3, 4-*b*]quinoline — PAQ4

Yellow crystals, 32 %, melting point (*m.p.*) = 206—207 °C. λ (cyclohexane) = 437 nm. ^{1}H NMR (300 MHz, $CDCl_3$): 8.51 (2H, *d*, J = 8.7 Hz, 2′-H, 6′-H), 8.21 (1H, *d*, J = 9.05 Hz, 8-H), 7.75 (1H, *d*, J = 8.7 Hz, 5-H), 7.74 (1H, *t*, J = 8.65 Hz, 6-H), 7.56 (2H, *t*, J = 8.0 Hz, 3′-H, 5′-H), 7.32—7.42 (1H, *m*, 5-H), 7.4 (2H, *d*, J = 8.0 Hz, 3″-H, 5″-H), 7.34 (2H, *d*, J = 8.0 Hz, 2″-H, 6″-H), 7.28 (1H, *t*, J = 7.4 Hz, 4′-H), 2.52 (3H, *s*, 4-C_6H_4-CH_3), 2.17 (3H, *s*, 3-CH_3). Elemental analysis for $C_{24}H_{19}N_3$: calculated: C — 82.49, H — 5.48, N — 12.03; found: C — 82.38, H — 5.26, N — 12.17.

3,6-Dimethyl-4-(4′-methylphenyl)-1-phenyl-1*H*-pyrazolo[3, 4-*b*]quinoline — PAQ5

Yellow crystals, 31 %, *m.p.* = 197—198 °C. λ (cyclohexane) = 438.5 nm. ^{1}H NMR (300 MHz, $CDCl_3$): 8.50 (2H, *d*, J = 8,7 Hz, 2′-H, 6′-H), 8.11 (1H, *d*, J = 8.7 Hz, 8-H), 7.57 (1H, *d*, J = 8.76 Hz, 7-H), 7.55 (2H, *t*, J = 8.0 Hz, 3′-H, 5′-H), 7.47 (1H, *s*, 5-H), 7.40 (2H, *d*, J = 8.23 Hz, 3″-H, 5″-H), 7.33 (2H, *d*, J = 8.23 Hz, 2″-H, 6″-H), 7.27 (1H, *t*, J = 7.4 Hz, 4′-H), 2.53 (3H, *s*, 4-C_6H_4-CH_3), 2.43 (3H, *s*, 6-CH_3), 2.14 (3H, *s*, 3-CH_3). Elemental analysis for $C_{25}H_{21}N_3$: calculated: C — 82.62, H — 5.82, N — 11.56; found: C — 82.51, H — 5.67, N — 11.32.

6-Bromo-3-methyl-4-(4′-methylphenyl)-1-phenyl-1*H*-pyrazolo[3, 4-*b*]quinoline — PAQ1

Yellow crystals, 32 %, *m.p.* = 205—206 °C. λ (cyclohexane) = 447 nm. ^{1}H NMR (300 MHz, $CDCl_3$): 8.46 (2H, *d*, J = 8.7 Hz, 2′-H, 6′-H), 8.04 (1H, *d*, J = 9.1 Hz, 8-H), 7.86 (1H, s, J′ = 2.0 Hz, 5-H), 7.75 (1H, *d*, J = 9.1, J′ = 2.0 Hz, 7-H), 7.55 (2H, *t*, J = 8.0 Hz, 3′-H, 5′-H), 7.40 (2H, *d*, J = 8.1 Hz, 3″-H, 5″-H), 7.31 (2H, *d*, J = 8.1 Hz, 2″-H, 6″-H), 7.28 (1H, *t*, J = 7.4 Hz, 4′-H), 2.53 (3H, *s*, 4-C_6H_4-CH_3), 2.13 (3H, *s*, 3-CH_3). Elemental analysis for $C_{24}H_{18}BrN_3$: calculated: C — 67.30, H — 4.24, N — 9.81; found: C — 67.05, H — 4.34, N — 9.76.

6-Methoxy-3-methyl-4-(4′-methylphenyl)-1-phenyl-1*H*-pyrazolo[3, 4-*b*]quinoline — PAQ3

Yellow crystals, 30 %, *m.p.* = 231—232 °C. λ (cyclohexane) = 448.5 nm. ^{1}H NMR (300 MHz, $CDCl_3$): 8.49 (2H, *d*, J = 8.7 Hz, 2′-H, 6′-H), 8.11 (1H, *d*, J = 9.2 Hz, 8-H), 7.54 (2H, *t*, J = 7.97 Hz, 3′-H, 5′-H), 7.43 (1H, *d*, J = 9.2 Hz, J′ = 2.8 Hz, 7-H), 7.36—7.37 (4H, 2″-H, 3″-H, 5″-H, 6″-H), 7.26 (1H, *t*, J = 7.4 Hz, 4′-H), 6.94 (1H, *s*, J′ = 2.8 Hz, 5-H), 3.73 (3H, s, 6-OCH_3), 2.52 (3H, s, 4-C_6H_4-CH_3), 2.14 (3H, s, 3-CH_3). Elemental analysis for $C_{25}H_{21}N_3O$: calculated: C — 79.13, H — 5.58, N — 11.07; found; C — 79.01, H — 5.51, N — 10.87.

3-Methyl-4-(4′-methylphenyl)- 6-phenoxy-1-phenyl-1*H*-pyrazolo[3, 4-*b*]quinoline — PAQ 2

Yellow crystals, 30 %, *m.p.* = 158—159 °C. λ (cyclohexane) = 446.5 nm.^{1}H NMR (300 MHz, $CDCl_3$): 8.50 (2H, *d*, J = 8.0 Hz, 2′-H, 6′-H), 8.20 (1H, *d*, J = 9.1 Hz, 8-H), 7.46—7.61 (3H, *m*, $H_{arom.}$), 7.24—7.38 (8H, *m*, $H_{arom.}$), 7.07 (1H, *t*, J = 7.3 Hz, 4‴-H in 6-OPh), 6.97 (2H, *d*, J = 8.5 Hz, $H_{arom.}$), 6.97 (2H, *d*, 2‴-H and 6‴-H in 6-OPh), 2.48 (3H, *s*, 4-C_6H_4-CH_3), 2.17 (3H, *s*, 3-CH_3). Elemental analysis for $C_{30}H_{23}N_3O$: calculated: C — 81.61, H — 5.25, N — 9.52; found: C — 81.52, H — 5.23, N — 9.43.

6-Chloro-3-methyl-4-(4′-methylphenyl)-1-phenyl-1*H*-pyrazolo[3, 4-*b*]quinoline — PAQ6

Yellow needles, 30 %, *m.p.* = 201—203 °C. λ (cyclohexane) = 446 nm. ^{1}H NMR (300 MHz, $CDCl_3$): 8.46 (2H, *d*, J = 8.7 Hz, 2′-H, 6′-H), 8.12 (1H, *d*, J = 9.0 Hz, 8-H), 7.68 (1H, s, J′ = 2.3 Hz, 5-H), 7.64 (1H, *d*, J = 9.0, J′ = 2.3 Hz, 7-H), 7.55 (2H, *t*, J = 8.0 Hz, 3′-H, 5′-H), 7.40 (2H, *d*, J = 8.1 Hz, 3″-H, 5″-H), 7.31 (1H, *d*, J = 8.1 Hz, 2″-H, 6″-H), 7.28 (1H, *t*, J = 7.4 Hz, 4′-H), 2.53 (*s*, 3H, 4-C_6H_4-CH_3), 2.14 (*s*, 3H, 3-CH_3). Elemental analysis for $C_{24}H_{18}ClN_3$: calculated: C — 75.09, H — 4.73, N — 10.95; found: C — 75.24, H — 4.86, N — 10.87.

Device preparation

Multilayer electroluminescence diodes were obtained according to the standard procedure [12]. They were prepared by co-dissolution of the matrix polymer (PVK) and PAQ's derivative in tetrahydrofuran (THF). The ratio of PAQ/PVK was maintained about 1:100 (this proportion was found experimentally to give the strongest emission in the LED structure). In the next step, the solution was deposited by spin-casting onto the glass substrate partially coated with a 100 nm layer of indum-tin oxide (ITO). The average thickness of the organic layer was measured to be about 50 nm. Finally a 10 nm thick calcium cathode was vacuum vaporated (< 1.33 · 10^{-4} Pa) and the whole was capped with a 100 nm aluminum protective layer. The overall structure of the device is presented in Fig. 1.

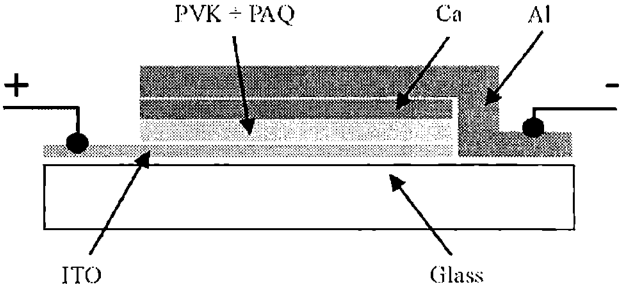


Fig. 1. LED's structure

LED estimation

The absorption spectra were recorded in tetrahydrofuran solution using a Shimadzu UV-VIS 2101 scanning spectrophotometer in the range 300—500 nm. Solution measurements were performed using standard 1 cm path length quartz cuvette for absorption spectrometry. PL and EL spectra were recorded by means of an Oriel Instaspec II monochromator/diode array detector. Quantum efficiency of photoluminescence (PL) was estimated using a Hamamatsu 1337 photodiode and Keithley 487 picoammeter with quinine sulphate as standard reference material. EL intensities were measured under 10 V using ITO/PVK + PAQ/Ca/Al cell.

RESULTS AND DISCUSSION

Absorption and PL spectra of the PAQ derivatives are shown in Fig. 2. Although the used spectrophotometer didn't allow to distinguish directly between PL and phosphorescence, this last one (if ever significant) had to be characterized by lifetime shorter than a tenth of second. Shapes of absorption and PL spectra are very similar for all investigated compounds. Maxima of the absorption spectra vary from 390 nm (PAQ6) to 411 nm (PAQ3). Maxima of the photoluminescence spectra are shifted towards the longer wavelengths by *ca.* 60—70 nm.

The recorded peaks of EL maxima cover 454—467 nm wavelength range (see Fig. 3). EL maximum at the shortest wavelength is observed for PAQ5 with -CH_3 as the

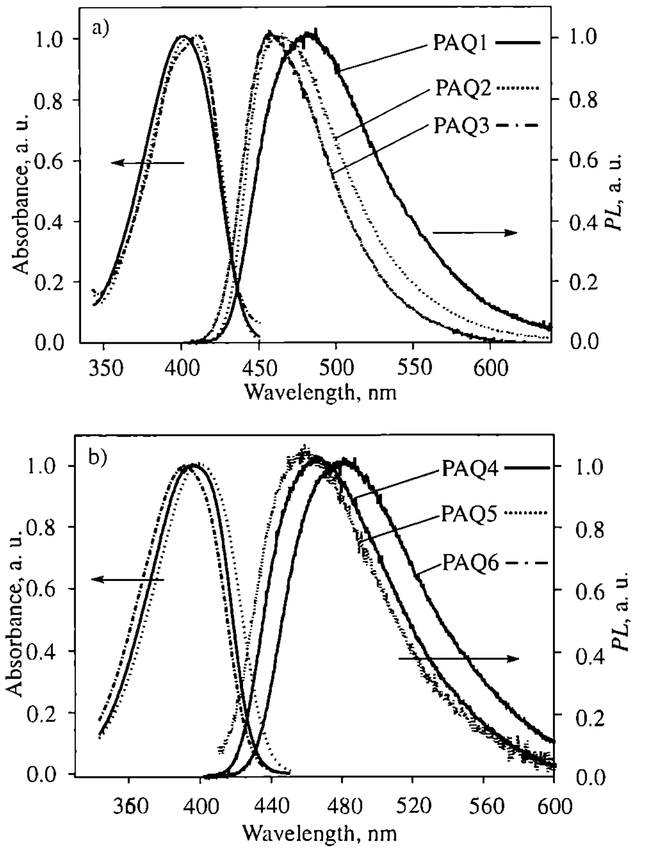


Fig. 2. Absorption and photoluminescence (PL) of PAQ samples: (a) PAQ1—PAQ3, (b) PAQ4—PAQ6

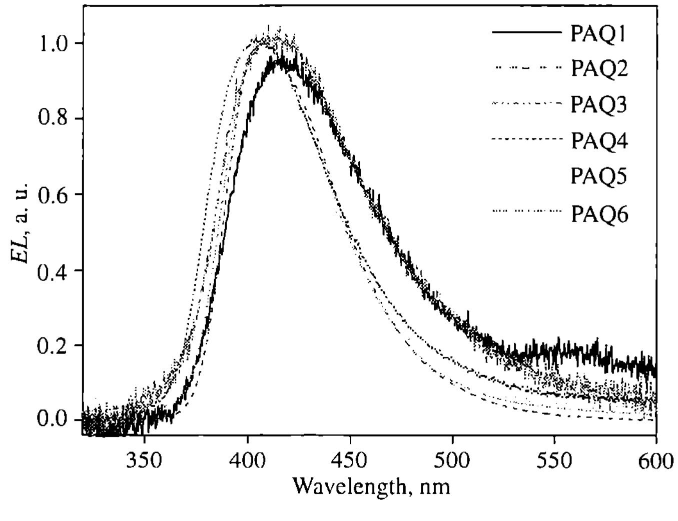


Fig. 3. Electroluminescence (EL) spectra of LEDs with active layer of various PAQ in PVK matrix

lateral group. On the other hand, EL maximum of PAQ1 (Br as lateral group) is shifted to longer wavelengths, relatively to its PL spectrum, only by 13 nm. Comparing the quantum efficiencies of PL and EL of PAQ1 and PAQ6 one can see the negative influence of heavy atom (Br, Cl) presence. The most efficient PL followed by best recorded EL was found in PAQ containing metoxy (PAQ3) and phenyloxy (PAQ2) side groups. It means that electron-donating substituents (-OC_6H_5, -OCH_3) enhance EL strength. In case of PAQ bearing an electron-acceptor (Cl, Br), EL efficiency was generally poor (see Table 1).

Table 1. Absorption photoluminescence (*PL*) and electroluminescence (*EL*) maxima and PAQs quantum efficiencies (φ_{Pl} and φ_{El} respectively)

Sample	Absorption, nm	*PL* nm	*EL* nm	Quantum efficiency, %	
				φ_{Pl}	φ_{El}
PAQ1	401	483	467	0.27	0.09
PAQ2	405	462	457	0.65	0.19
PAQ3	411	456	457	0.83	0.27
PAQ4	396	465	455	0.58	0.008
PAQ5	400	459	454	0.77	0.02
PAQ6	391	481	464	0.42	0.009

Figure 4 (electroluminescence — current LED's characteristics) shows that EL values of PAQ3 or PAQ4 are rather high.

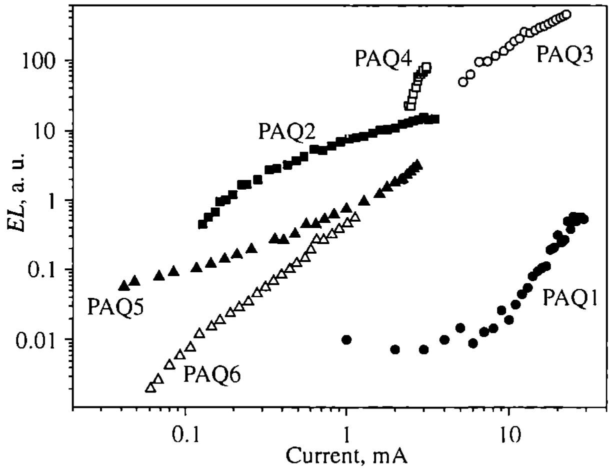


Fig. 4. Dependence of electroluminescence (EL) on the current of PAQ based LEDs

Analysis of the course of a dependence EL ≈ f (*j*) (*j* — current density) shows that for PAQ1, PAQ5 and PAQ6 an electroluminescence can be described as follow: EL j^n, where *n* is close to 2 [1]. This phenomenon can be explained on the basis of a model of injection controlled electroluminescence (ICEL) [13]. In the case of characteristics other types of PAQ it is difficult to do a simple interpretation.

So, from the results presented, testifing to dependence of pyrazoloquinolines electroluminescence properties on the substituent, it is clear that both the position of electroluminescence maxima as well as quantum of efficiency yield can be controlled.

ACKNOWLEDGMENTS

This work was partly supported by Polish State Committee for Scientific Research (KBN), grant No 4 T08E 097 25.

REFERENCES

1. Kalinowski J.: *J. Phys. D: Appl. Phys.* 1999, **32**, R175.
2. Schott M.: *C. R. Acad. Sci. Paris ser. IV* 2000, **1**, 381.
3. Dentan V., Vergnolle M. Facoetti H., Vériot G.: *C. R. Acad. Sci. Paris ser. IV* 2000, **1**, 425.
4. Michaelis A., Liebigs J.: *Ann. Chem.* 1911, **1**, 385.
5. Nizioł J., Danel A., Gondek E., Armarys P., Sanetra J.: Macromol. Symp., to be published.
6. Tao Y. T., *et al.*: *Chem. Mater.* 2001, **13**, 1207.
7. Bogdał D., Stępień I., Sanetra J., Gondek E.: *Polimery* 2003, **48**, 111.
8. Brack A.: *Liebigs Ann. Chem.* 1965, **681**, 111.
9. Hennig L., Müller T., Grosche M.: *J. Prakt. Chem.* 1990, **332**, 693.
10. Chaczatrian G., *et al.*: *ARKIVOC* 2001, **2**, 1.
11. Chaczatrian K., Chaczatrian A., Danel A., Tomasik P.: *Polish J. Chem.* 2003, **77**, 1141.
12. Sanetra J., Barta P., Nizioł S., Chrząszcz R., Pielichowski J.: *Synth. Met.* 1998, 123.
13. Kalinowski J.: "Multiphoton and Light Driven Multielectron Processes" in: "New Phenomena, Materials and Applications", (Eds. Kajzar F., Agranovich M. V.), vol. 79, Kluwer Academic Publishes 2000, p. 325—344.

Received 24 IV 2003.