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Light emitting diodes based on pyrazoloquinoline derivatives

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Light emitting diodes based on pyrazoloquinoline derivatives were synthesized. Principal role of dye chromophore static dipole moment's values for the light emitting diodes possessing single layered architecture ITO/PVK:pyrazoloquinoline/Ca/Al is explored. It is established that pyrazoloquinoline dye chromophore with lower state dipole moments favor enhanced output electroluminescence. It may be caused by decrease of nonradiative recombination for the dyes with lower dipole moments. Parameters of the observed electroluminescence are compared with the photoluminescence, current-voltage features and parameters of the state, transitions and excited dipole moments of the dye chrmophore. The performed absorption, photoluminescent and carrier kinetics investigations of the chromophore indicate a principal possibility to operate by the carrier kinetics by variation of the value of their state dipole moments without a necessity of variation by energy positions of the HOMO/LUMO levels.

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Keywords: Light emitting diodes, 1*H*-pyrazolo [3,4-*b*] quinoline derivatives, Electroluminescence, Photluminescence

1. Introduction

Over the past several years, organic polymers with incorporated chromophore dyes have demonstrated potential for application in high-advanced light-emitting and photovoltaic devices. The features that make these materials so attractive are high spectral tunability, multi-functional illumination etc. Varying the parameters of the polymer matrix or of incorporated organic dye chromophore one can achieve the desired degree of light emitting brightness, quantum efficiency and high energy efficiency etc.

Search and design of new materials for the light emitting diodes (LED) possessing desirable and reliable electroluminescent features is one of the principal goals for modern engineering of LED. One of effective way to create effective LED are high performed polymeric LED with incorporated organic chromophore dyes. The polymers are used as host ensuring high effective carrier transport and the incorporated molecule are served as effective light emitting elements. One of the goals of the design for such LED is to ensure the optimal conditions for injection of the holes and electrons from the electrodes to the transport polymer matrix.

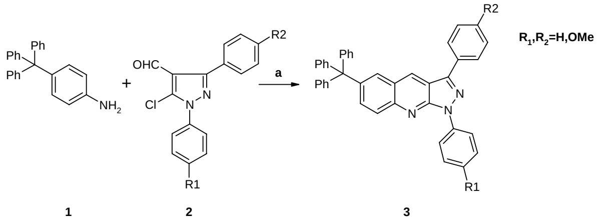
One of a limiting factor for the more quick application of the LED is a misbalance in charge injection [1]. Usually such improvement is achieved during design of multi-layered devices consisting of an emitting layer deposited between hole (ITO) and electron Ca(Al) injectors [2]. However, complication in a fabrication of such devices favors a dozen of investigations devoted to the single layered LED [3]. Recently pyrazoloquinoline derivatives have been applied as chromophore for single layered LED [4,5]. These dyes possess relatively small sizes compared to the traditionally used.

Principal role in the LED carrier kinetics plays an evolution of the excitonic states after excitation [6]. Intermolecular (chain-polymer) and inter-chain coupling play crucial role for intermolecular relaxation dynamics during moving of excitons by host polymer chains. An efficiency of these processes is determined by values of the state dipole moments of the guest chromophore and the host polymer matrix. These Coulomb-like interactions form the excitonic states in the forbidden optical energy gap which are a source of the trapping nonradiative losses of the corresponding excitons. Together with polaronic states created by electron-vibration self-localised states these states are efficient trapping levels for the free charge carrier (electron and hole) kinetics. As a consequence the moving carriers may be trapped by the corresponding levels without an emission which may substantially quench an efficiency of electroluminescence. So one can expect that the lower state dipole moments would be more desirable for the LED. However, there is a factor of chromophore aggregation causing red shift luminescence with appropriate emission quenching occurring at low state dipole moments. Principal goal is a substantial modification of the dye chromophore state dipole moments without changes of energy position for the principal HOMO and LUMO levels. In the present work we will investigate electroluminescent parameters for several modified pyrazoloquinoline molecule possessing substantially different state dipole moments. We will explore two matrices – polyvinylkarbazole (PVK) and polysilane (PSS) (for comparison). In the Section 2 we present technology of sample synthesis of the dye chromophore based on pyrazoloquinoline and preparation of the corresponding light emitting devices. Section 3 describes the principal experimental results (current-voltage, electroluminescence, photoluminescence etc.) and comparison with their state dipole moments.

2. Experimental part

The luminophors for OLED were prepared by reaction of trityl aniline **1** with aldehydes **2** according to procedure depicted on the scheme 1. The reagents were slowly heated within the temperature range 140-190 ºC. At 140-160 ºC water was eliminated due to Shiff base formation and at 180 ºC the rearrangement occurs with the elimination of HCl. The reaction was finished when HCl was no detected (indicator paper). Aldehydes **2** were prepared by Vilsmeier-Haack formylation ($POCl_3$/DMF) of pyrazolones.

All reagents were purchased from commercial suppliers (Merck and Aldrich) and were used without further purification. The solvents were purchased from POCh (Polish chemicals supplier). NMR spectra were recorded on a Varian VXR 300 spectrometer in $CDCl_3$ solution. The elemental analyses data were in agreement with calculated values (±0.3%).



Scheme 1. a) heating, 150-190 ºC.

p-Trityl aniline (1 mmol, 0.335 g) **1,** 5-chloro-4-formylpyrazole (0.01 mol) **2** with a few drops of sulfolane were heated together at 150-190 ºC for 50 minutes. The melt was boiled with ethanol (20 mL) and the yellow precipitate was filtered off. The solid was dissolved in chloroform and filtered through short layer of alumina (Merck 60, neutral, II-III Brockmann). The final purification was performed on silica gel (Merck 60, 70-230 mesh) using toluene and ethyl acetate (3:1) as eluent.

Mol1 1-(p-Methoxyphenyl)-3-phenyl-6-trityl-1*H*-pyrazolo[3,4-*b*]quinoline 3a

Bright yellow crystals were obtained with mp 284-286 ºC , yield 56 %.

^{1}H NMR(300 MHz, $CDCl_3$): 8.82(s, 1H, 4-H); 8.45,8.42(AA’, 2H, 2,6-H_{1Ph}); 8.16(d, *J* = 9.1Hz, 2H, 2,6-H_{2Ph}); 8.02(d, *J* = 9.1Hz, 1H, 8-H); 7.93(d, *J* = 2.1 Hz, 1H, 5-H); 7.62-7.50(m, 4H, 7-H, 3,4,5-H_{2Ph}); 7.34-7.27(m, 15H); 7.15, 7.12(BB’, 2H, 3,5-H_{1Ph}); 3.93(s, 3H, OMe).

Mol2 3-(p-Methoxyphenyl)-1-phenyl-6-trityl-1*H*-pyrazolo[3,4-*b*]quinoline 3b

Bright yellow crystals, mp 305-309 ºC , yield 67%.

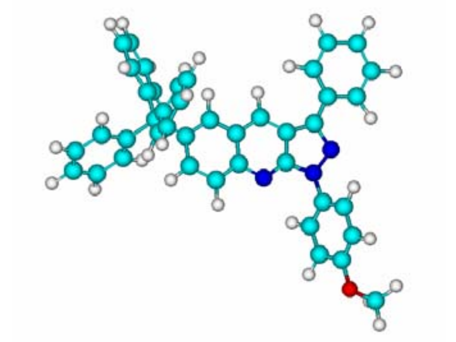
^{1}H NMR(300 MHz, $CDCl_3$):8.78(s, 1H, 4-H); 8.62(d, *J* = 7.6 Hz, 2H, 2,6-H_{1Ph}); 8.12, 8.09(AA’, 2H, 2,6-H_{2Ph}); 8.04(d, *J* = 9.2 Hz, 1H, 8-H); 7.93(d, *J* = 2,1 Hz, 1H, 5-H); 7.62-7.55(m, 4H); 7.35-7.27(m, 15H); 7.14, 7.11(BB’, 2H, 3,5-H_{2Ph}); 3.96(s, 3H, OMe).

Mol3 1,3-(p-Methoxyphenyl)-3-phenyl-6-trityl-1*H*-pyrazolo[3,4-*b*]quinoline 3c

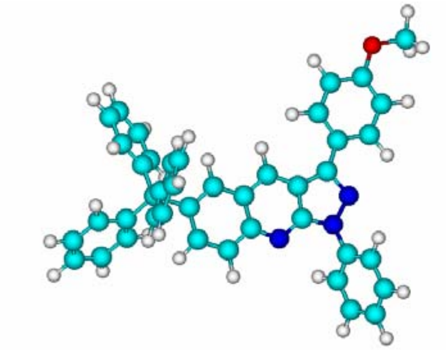
Bright yellow crystals, mp 245-6 ºC, yield 53%.

^{1}H NMR(300 MHz, $CDCl_3$):8.78(s, 1H, 5-H); 8.41,8.37(AA’, 2H); 8.06, 8.03(AA’, 2H); 8.98(d, *J* = 9.2Hz, 1H, 8-H); 7.88(d, *J* = 2.2 Hz, 1H, 5-H); 7.51(dd, *J* = 9.2Hz, 2.3 Hz, 1H, 7-H); 7.30-7.15(m, 15H); 7,11-7.07(2×BB’, 4H); 3.90(s, 3H, OMe); 3.89(s, 3H, OMe).

Mol1



Mol 2



Mol 3

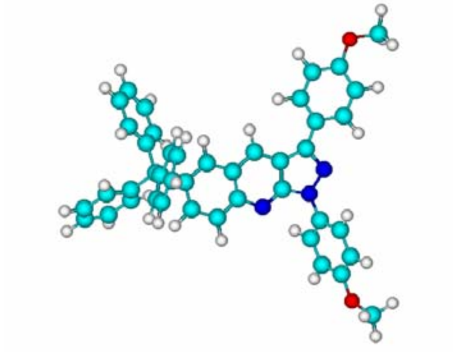


Fig. 1. Principal chemical formulas of the investigated pyrazoloquinoline dye molecule.

3.3. Principal parameters of the LED

The EL devices possessing the structure: indium tin oxide (ITO)/PVK: PAQ-D/Ca/Al (see Fig. 2) were fabricated by spin-coating and thermal vacuum deposition technique. They were prepared by co-dissolution of the polymer PVK matrix and the investigated PAQ derivative in THF. The ratio of PAQ/PVK was equal to about 1:100. Afterwards, the solution was deposited by spin-casting method onto the BK7 glass substrate coated with a 100 nm layer of ITO. The average thickness of the organic layer was equal to about 100 nm. The active surface of the device was equal to about 7 mm^2. The typical morphology of the active emissive layers is given in the Fig. 2 a and 2 b.

After a 10 nm thick calcium cathode was deposited by vacuum evaporation and the whole was capped with a 100 nm aluminum protective layer.

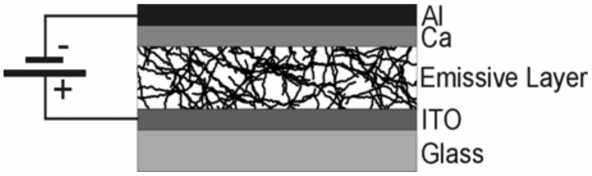


Fig. 2. The sketch of the used LED.

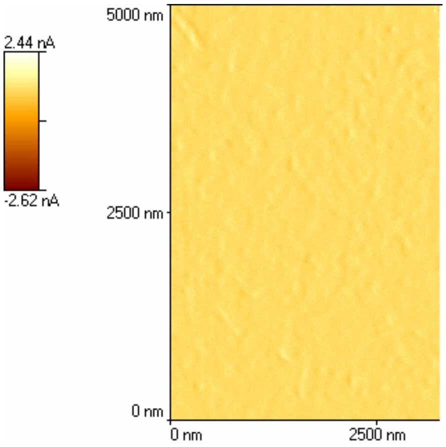


Fig. 2 a. Typical AFM image for PVK matrix.

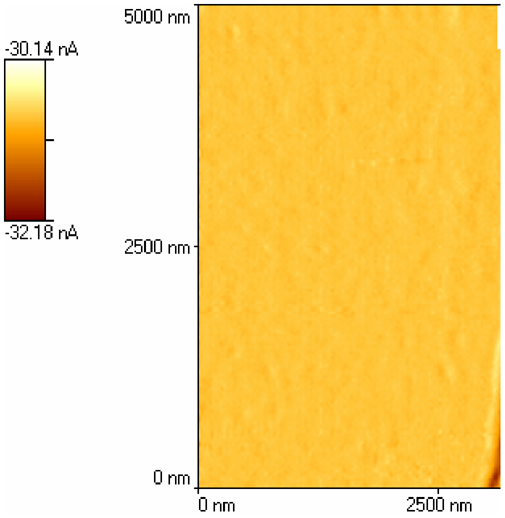


Fig. 2 b. Typical AFM image for PSS matrix.

3. Results and discussion

In the Fig. 3 UV-VIS absorption spectra of the three investigated molecule embedded into the tetrahydrofuran (THF) solution are presented. There are two strong spectral maxima situated at wavelengths 240 nm and 276 nm. The spectra are similar for different dye chromophores. More sensitive to the chromophore type are the first long wavelength UV-VIS spectral bands. One can see a blue spectral shift of the first long wavelength maxima during undergoing through Mol 3 –>Mol 2 –> Mol 1 for spectral range 430 nm – 405 nm. To understand the origin of this spectral shift we have performed DFT calculations within the B3LYP method to evaluate HOMO – LUMO energy distance and of the corresponding state and transition dipole moments for isolated molecule. The corresponding data are given in the Table 1.

Table 1.

Mol.	State dipole moments	Excited dipole moments	$\lambda_{\max,\ nm}$	HOMO	EL [arb.units]
1	0.77±0.03 D	1.69±0.03 D	385.1 nm	-6.18 eV	1.9
2	0.34±0.03 D	2.82±0.03 D	387.9 nm	-6.07 eV	3
3	1.36±0.03 D D	3.17±0.03 D	395.7 nm	-6.02 eV	0.89

Comparing the experimental Fig. 3 and the calculated parameters of the first absorption maxima one can emphasize a sufficiently good agreement in their spectral positions. The changes in the optical spectra going from solution to the films are caused by the interactions of transition dipole moments of the molecules. The molecules tend to aggregate in the PVK or PSS matrix.

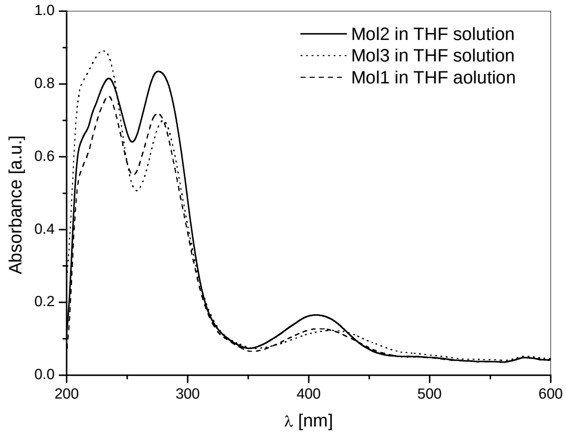


Fig. 3. UV-VIS absorption spectra of the investigated chromophore molecule in the THF.

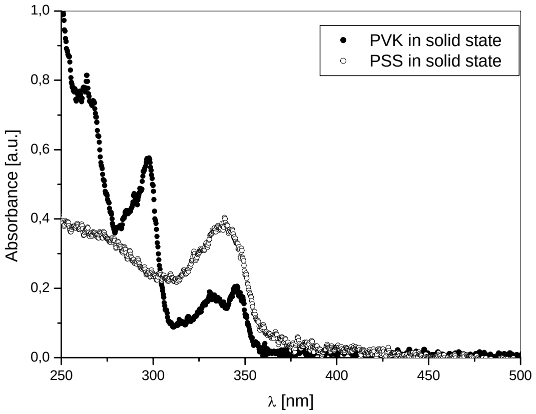


Fig. 3 a. Typical absorption spectra of the pure PVK and PSS matrices.

After incorporation of the investigated dye chromophore into the PVK and polymethyl- phenyl -silane matrices the observed spectra have shown substantial rearrangement (see Fig. 2 and Fig. 3). For the clarification of the role played by polymer matrix in PVK and PSS matrices it is necessary to analyse the obtained results in a more detailed way. In particular, the two (almost a same by intensity) UV bands in the THF are split into two non-equivalent by intensity absorption bands – at about 275 nm and 310 nm (for the PVK) and – at 290 nm and 340 nm for polisylane (PSS) matrix. For all molecules, the higher spectral bands in polymer host are always red shifted reflecting dye aggregate formation. Moreover, for the **Mol. 2** and **Mol. 3** these second peaks disappear at all. This fact may reflect substantial changes of transition dipole moments during the aggregation with respect to the solvating isolated chromophore. This may be crucial during investigations of the carrier mobility and exciton transfer determined by trapping due to the chromophore-polymer interactions [7]. Therefore, this factor is crucial for the energy of the exciton recombination barrier with respect to the electrodes.

For comparing the influence of the PVK and PSS matrices it is necessary to emphasize that for the PSS matrix there is a low influence of the matrix on the spectral position of the principal absorption which may indicate on the lower degree of dye chromophore aggregation. However, for the PVK matrices it is observed substantial spectral shift of the spectral maxima up to 30 nm towards shorter wavelengths and may indicate on the higher degree of the aggregation. As the mentioned optical transitions play major role, we will pay more attention to the PVK based molecules, which potentially enhance interactions between the polymer chains and the chromophores.

From the Fig. 4-8 one can see that despite different spectral positions of the particular absorption maxima of photoluminescence (PL) excited by mercury lamp one can observe clear low spectral dispersion, which is Stokes red-shifted with respect to the absorption bands from 80 nm up to 150 nm. So, an influence of dipole-dipole and electron-ionic interactions may be substantial here [7]. Generally, all the measured PL spectra are asymmetric and less broadened for PVK matrix compared to the PSS ones.

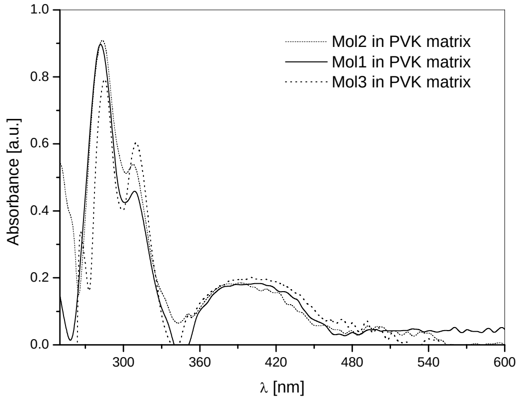


Fig. 4. VUV-VIS absorption spectra of the chromophore in different matrices.

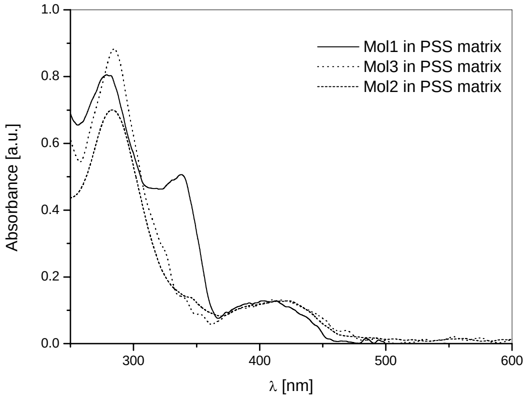


Fig. 5. UV-VIS absorption spectra for the investigated molecule in the PSS matrices.

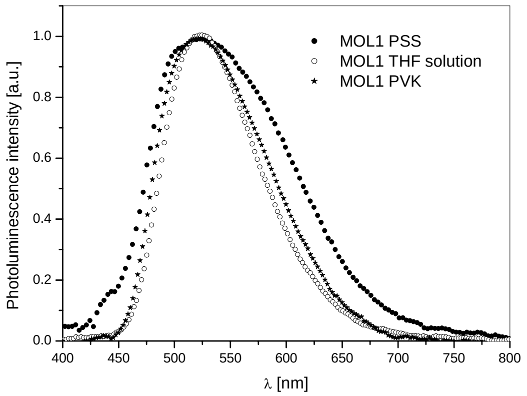


Fig. 6. PL spectra of the MOL. 1 in the different matrices.

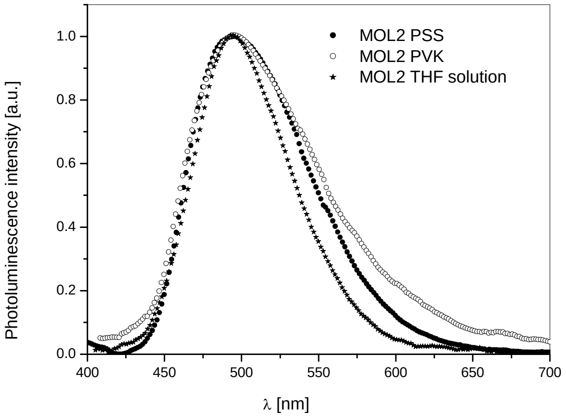


Fig. 7. PL spectra of the MOL. 2 in the different matrices.

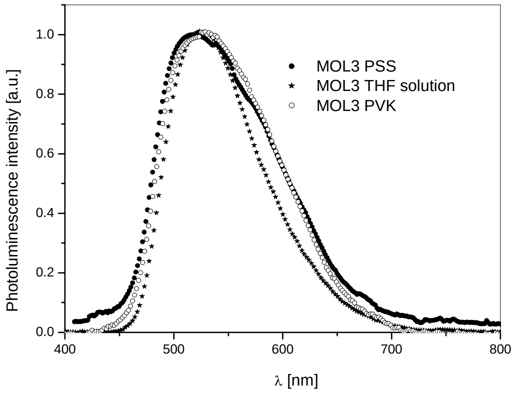


Fig. 8. PL spectra of the MOL. 3 in the different matrices.

For convenience of readers several comparisons of experimentally measured emission parameters are gathered in the Table 2. There are presented the PL results obtained for the solvents with different polarities. From the Table 2 it is clear that maximal PL efficiency is achieved for the hexan solvent (less polar). The same holds for the fluorescence lifetimes. Upon applying more polar solvent one can see a quenching of the PL efficiency and decrease of fluorescence life times. This fact confirms the principal role of the matrix polarizability for the kinetics of the carriers during the emission. Several exceptions are observed for the Mol. 2. It may be a consequence of substantially lower dipole state moment value for the Mol. 2 compared to other ones. As a consequence the transfer of excitation determining the recombination becomes relatively low.

Tabele 2. Fluorescence lifetimes τ (ns) quantum yields Φ photoluminescence and position of the maximum of photoluminescence (PL) and electroluminescence (EL).

Compounds	Solvent	τ (ns)	Φ_{PL}	PL [nm]	EL [nm]
Mol 1	Hex	21.65	1.010	489	499
	THF	9.65	0.284	529	
	ACN	2.96	0.097	540	
Mol 2	Hex	17.40	1.026	462	491
	THF	21.00	1.020	494	
	ACN	27.50	1.010	497	
Mol 3	Hex	22.45	0.830	491	505
	THF	15.20	0.470	524	
	ACN	4.20	0.110	553	

The obtained data indicate a possibility to use the PVK matrix as more preferable compared to the PSS ones. Further investigations should be concentrated on the single layered LED with PVK matrix.

Current-voltage dependences for the three types of the LED configurations are given in the Fig. 9. One can see that occurrence of the current in visible earlier for the molecule 1 (at above 2 V) and only for voltages above 8 V it is almost the same as current for the Mol. 2. It correlates with the absorption behavior for the mol. 2. According to the Table 1, one may conclude that principal role in this case is played by the values of the dye chromophore dipole moments effectively forming the trapping nonradiative levels re-distributing the nonradiative losses. Occurrence of the onset at about 6 V and observation of the strong onset at 6 V may indicate on the presence of the mentioned trapping levels which favor carrier transport, however quenching the output emission. Below 6 V the carrier jumps are low probable and this fact may confirm an absence of the effective carrier transport at low applied voltages.

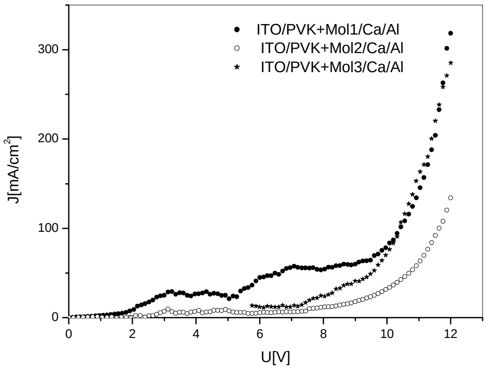


Fig. 9. Current-voltage dependences for the three chromophore dyes.

For the entire dye molecule one can see several staircase-like jumps of current at voltages below 6 V (see Fig. 9). Substantial current increase corresponding to effective hole injection occurs above 10 V. So applying an external bias voltage one can operate by the carrier kinetics between the trapping levels.

Following the features of the Mol. 2 one can expect that the beginning of the EL should start earlier than for other molecule. This fact is confirmed by Fig. 10 and 10 a. For convenience of carrier transport analysis EL-current dependences are presented in the logarithmic scale (Fig. 11). One can see substantial advantages of the Mol 2 (possessing lower ground state dipole moments) with respect to other molecules is shown. The large power index (about 8.5) in the current-voltage dependences may indicate the substantial role of the trapping states in the carrier kinetics. Comparison of the Fig. 9 and Fig. 10 unambiguously shows that the principal role in the efficiency of the EL is played by the state dipole moments (see Table 1) and not by the excited state dipole moments. The delayed current-voltage features reflect the absence of nonradiative trapping levels for the molecule with the lower state dipole moments. At the same time there is not a correlation between the values of the excited dipole moments and the efficiency of the corresponding EL.

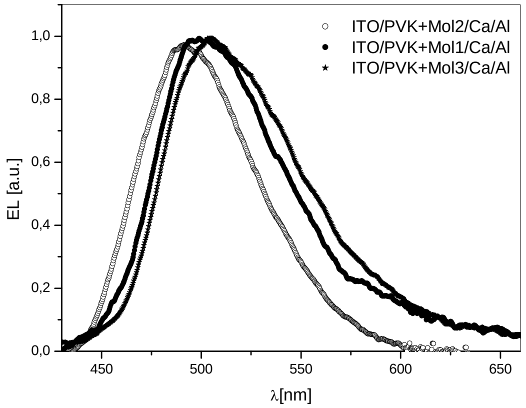


Fig. 10 a. Typical spectral dependences of the EL.

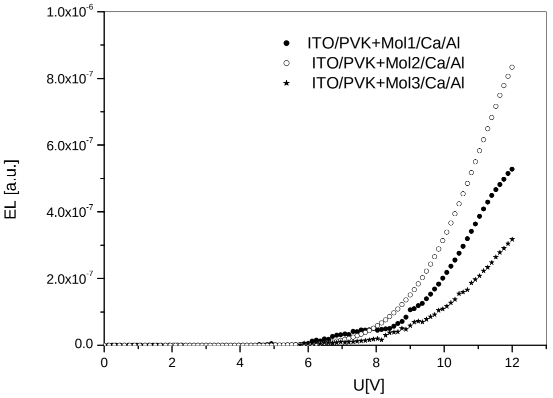


Fig. 10. Electroluminecent dependences for the three chromophores.

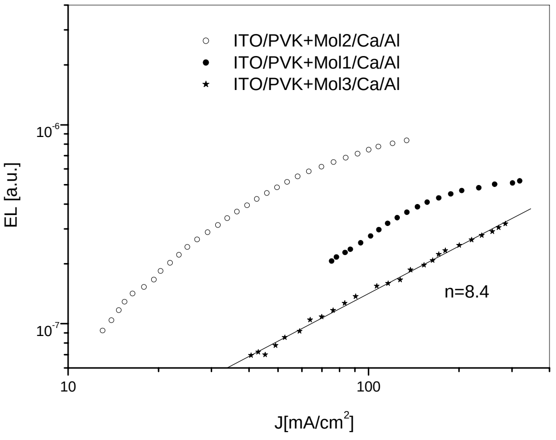


Fig. 11. EL-current dependences of the EL.

The obtained EL spectra are more broadened than the PL ones. Charge trapping levels play substantial role in the observed EL processes for thick emission layers.

For higher electroluminescence output, the high efficient exciton recombination is desired. That means that the nonradiative recombination should be quenched. The recombination probability is related to the current density of holes, the film thickness, the applied electric field E, and the electron/hole mobility [8]. Low recombination of excitons in luminescence layer suppresses the EL efficiency. Sometimes quenching of the generated excitations is observed nearby the electrode interface layer and may lead to the suppression of the EL efficiency [9]. In our case the most crucial parameter is the state dipole moment, which by interacting with the polymer chains forms the intra-band trapping levels effectively re-distributing the nonradaitive losses. Moreover, several role also may play nano-confined effects [10].

4. Conclusions

During investigations of the electroluminescent and current voltage dependences of the single layered LED in ITO/PVK:PQ/Ca/Al architecture it was shown the principal role of the value of state chromophore (pyrazoloquinoline) dipole moments on the kinetics of the excitons and their recombinations that determine the electroluminescence. It is clearly shown that the pyrazoloquinoline dye chromophores possessing substantially lower dipole moments lead to larger output electroluminescence. It may reflect lower nonradiative losses caused by the exciton trapping levels in the optical energy gap. The correlation between the bias onset and occurrence of the electroluminescence confirms this prediction about the role of chromophore-polymer interactions. The power index about 8.5 indicates the principal role of the trapping levels in the observed kinetics.

Acknowledgements

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