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Star-burst 1*H*-pyrazolo[3,4-*b*]quinoline as chromophore for light emitting diodes and photovoltaic devices

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Abstract: The current-voltage and electroluminescent features of the novel star-burst 1*H*-pyrazolo[3,4-*b*]quinoline chromophore have shown their potential applications as materials for light emitting diodes. The electroluminescence covers the white light spectral range from 420 nm up to 610 nm and achieves maximal value about 18 Cd/m² at biased voltage 23 V. The achieved PV efficiency was equal to about 0.08 %.

1. Introduction

In the early stage of electronic devices was fabricated prevailingly from inorganic materials based on silicon and germanium [1]. But organic materials due to chipper production costs can demonstrate also some conductive properties. The intense development of conductivity studies of organic materials started in 1960 when the synthesis of some anion-radical derivatives of tetracyano-*p*-quinodimethane TCNQ was performed [2]. At present we can encounter organic transistors, sensors, molecular wires, photovoltaics devices or organic displays. In the last case a tremendous progress can be observed from the pioneering famous Tang's paper published in 1987 [3]. At present organic displays are very popular in cameras, lightning panels, electric razor, MP3 players or small TV screens. Photonic energy is probably the cheapest and the most abundant and available source of energy. Unfortunately almost all commercial products available to us use inorganic materials based on silicon as single crystals or in the form of polycrystalline mass. We should expect rapid development of organic photovoltaic (PV) devices in the nearest future because of shrinking the natural resources of energy like oil or coal so the progress in the field of organic photovoltaic devices is growing in the last years too. The most important advantage of inorganic materials is their environmental resistance towards oxidation and moisture. They possess significant thermal stability. On the other hand one of the main obstacles as far as inorganic materials is

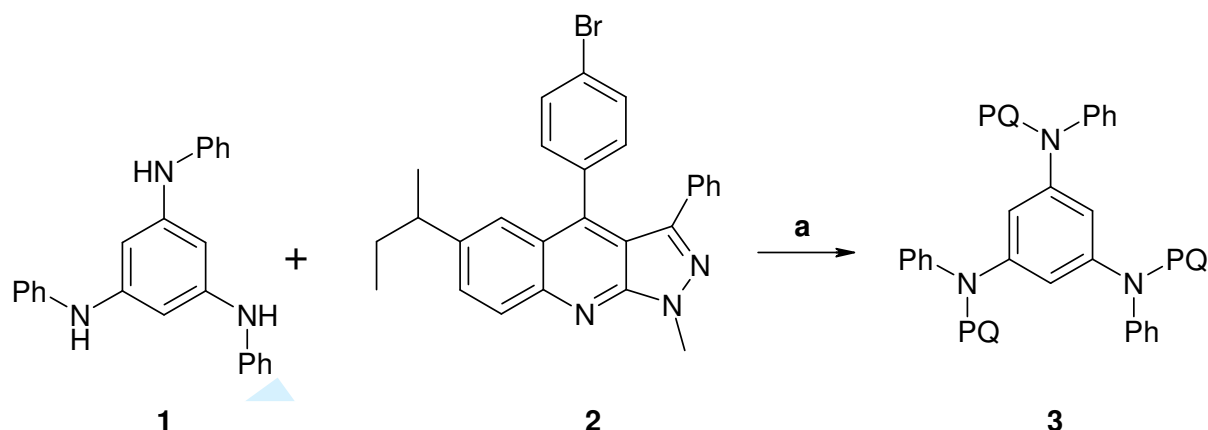
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3 concerned is their cost of fabrication. In some cases the technologies are based on single
4 crystal materials which are difficult to prepare. On the other hand one of the main drawbacks
5 in organic electronics is the instability of organic materials. Small organic molecules tend to
6 crystallize readily and this feature can be cause of device failure. This process can be slow but
7 in some cases it may be accelerated due to heat evolved during device operation. The second
8 reason is the influence of moisture and oxygen so devices must be encapsulated.
9

10
11 One of the solutions to prevent crystallization of organic materials is the proper
12 structural architecture. The main classes of amorphous and thermally stable compounds are
13 *spiro* [4], *cardo* [5], tetraphenylmethane based molecules [6] and *star-burst* [7] ones.
14

15
16 In our investigations of electroluminescent devices we successfully applied 1*H*-pyrazolo[3,4-
17 *b*]quinolines which are highly emissive luminophores [8]. These compounds melt in vast
18 range of temperatures reaching up to 420 °C and can be easily modified to enhance
19 amorphous properties. In the present work we report the synthesis of some *spiro*, *cardo* and
20 *star-burst* type systems. And we explore their possibility to use as .
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28 **2. Experimental**

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30 The synthetic procedure is outlined on scheme 1. Amine **1** was prepared from phloroglucine,
31 aniline hydrochloride by heating at 190 °C in aniline according to literature procedure[9] .
32 Pyrazoloquinoline **2** are prepared in a single step from aromatic aldehyde, substituted aniline
33 and pyrazolone [10]. All of these compounds are commercially available. *Star-burst* type
34 compounds **3** are prepared by palladium catalyzed amination of bromoderivative **2** according
35 to methods described for amination of halogen substituted aromatic compounds [11,12,13].
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37 In summary the final compound can be obtained in 2-3 stages synthetic procedure. In the case
38 of organic electronic materials synthesis the whole procedure should be as short as possible
39 from the economical point of view.
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Scheme 1. a)

Synthesis

The chemicals were purchased from commercial suppliers (Merck and Aldrich). Solvents were bought from POCH (Polish chemical company). ^1H NMR spectra were recorded on Varian VXR 300 spectrometer. MS spectra were measured on Esquire 3000 ESI-TRAP MS (Bruker Daltonics, Bremen, Germany) apparatus using Shimadzu UV-Vis 2101 scanning spectrophotometer in range 200–500 nm with spectral resolution of 1 nm.

N,N',N'' – Triphenylbenzene-1,3,5-triamine **1**

This compound was prepared from phloroglucine dihydrate (0.01 mol, 1.6g), aniline hydrochloride (0.033 mol, 4g) and aniline (20 ml) by heating the reactants at 180-190 °C according to literature procedure[9]

(±)-6-*sec*-Butyl-4-(*p*-bromophenyl)-1-methyl-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline **2**

p-Bromobenzaldehyde (0.01 mol, 1.40 g), *p-sec*-butylaniline (0.01 mol, 1.5 g) and 2-methyl-5-phenyl-2,4-dihydropyrazol-3-one (0.01 mol, 1.73g) were heated at 180-190 °C in 10 mL of diethylene glycol for 2 hours. After cooling the reaction mixture was diluted with ethanol (15 mL) and the precipitate was filtered off, dried and purified on column packed with aluminum oxide using toluene as eluent to remove tars. The final purification was done on column packed with silica gel (Merck 60, 70-230 mesh) using toluene:ethyl acetate 3:1.

Bright yellow crystals, 33% yield, mp 170-171 °C.

^1H NMR (300 MHz, CDCl_3 , δ ppm): 8.13(d, $J = 8.9\text{Hz}$, 1H, 8-H); 7.65(dd, $J = 8.9\text{Hz}$, 2.0Hz, 1H, 7-H); 7.57(d, $J = 2.0\text{Hz}$, 1H, 5-H); 7.25-7.18(m, 3H); 7.14-7.02(m, 6H); 4.3(s, 3H, N-Me); 2.67(sextet, $J = 6.9\text{Hz}$, 1H); 1.64(quintet, $J = 7.1\text{Hz}$, 2H); 1.24(d, $J = 6.9\text{Hz}$, 3H); 0.80(t, $J = 7.3\text{Hz}$, 3H).

Anal. Cald for $\text{C}_{27}\text{H}_{24}\text{BrN}_3$: C 68.94 H 5.14 N 8.93. Found C 68.78 H 5.01 N 8.87.

Star-burst PQ **3**

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3 A dry three-neck flask (25 ml) equipped with a magnetic stirrer bar, septum and a condenser
4 with a nitrogen inlet-outlet was charged with equipped *N,N',N''*-Triphenylbenzene-1,3,5-
5 triamine **1** (100 mg, 0.28 mmol), pyrazoloquinoline **2** (522 mg, 1.1 mmol), Pd₂(dba)₃ (10.2
6 mg), (2-biphenyl)di-*tert*-butylphosphine (6.6 mg) and *tert*-BuOK (200mg).The flask was
7 evacuated and flushed with nitrogen. Dry and de-aerated toluene (10 mL) was added. The
8 reaction mixture was heated at 100 °C for 24 hours. The mixture was diluted with ether (30
9 mL) filtered through Cellite and concentrated in vacuo. The crude material was purified by
10 column chromatography (Merck Silica-gel 60, 70-230 mesh; toluene – ethyl acetate 3:1).
11 Analytical sample was prepared by preparative thin layer chromatography.

12 Yellow powder, 200mg, 46%, mp 184-5 °C.

13 ¹H NMR(300 MHz, CDCl₃, δ ppm): 8.15(d, *J* = 8.4Hz, 3H); 7.70(d, *J* = 2.0Hz, 3H); 7.65(dd,
14 *J* = 9.0Hz, 2.0Hz, 3H); 7.30-7.25(m, 14H); 7.20-6.96(m, 28H); 6.76(s, 3H, 2,4,6-H_{Ph} core);
15 4.34(s, 9H); 2.66(sextet, *J* = 6,9Hz, 3H); 1.58(m, 6H); 1.23(d, *J* = 6,9 Hz); 0.79(t, *J* = 7,1Hz,
16 9H). MS(ES): (m/z): 1520 (M⁺).

3. Calculation procedure

17 All the quantum chemical computations were done using HyperChem-7.5 computer
18 package. Te general procedure was similar to the described in the Ref. 10 . During the first
19 step we have performed the geometry optimization by molecular mechanics force filed
20 (MM+), which is the most general and frequently used method for molecular mechanics
21 calculations developed principally for organic molecules. The geometry optimization and
22 the calculation of HOMO and LUMO were accomplished by using a semi-empirical
23 quantum chemical method: AM1.The principal results was an establishment of a fact that
24 the total ground state dipole moment is equal to about 5.6 D.
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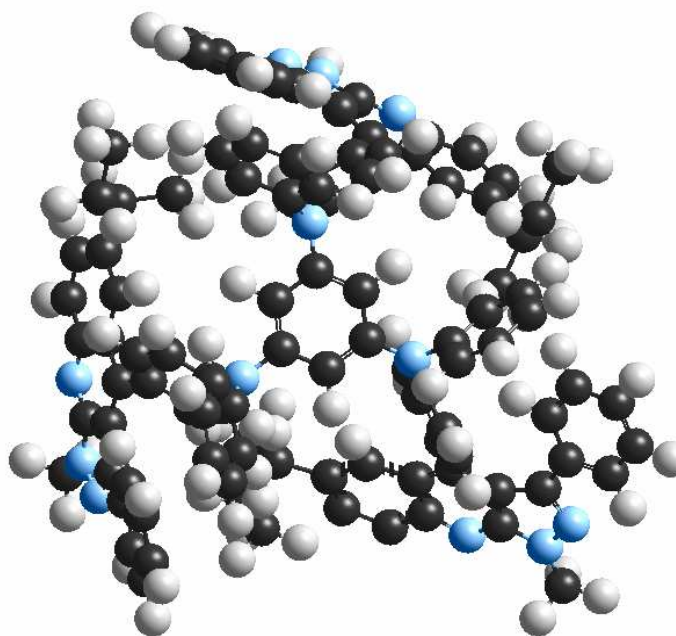
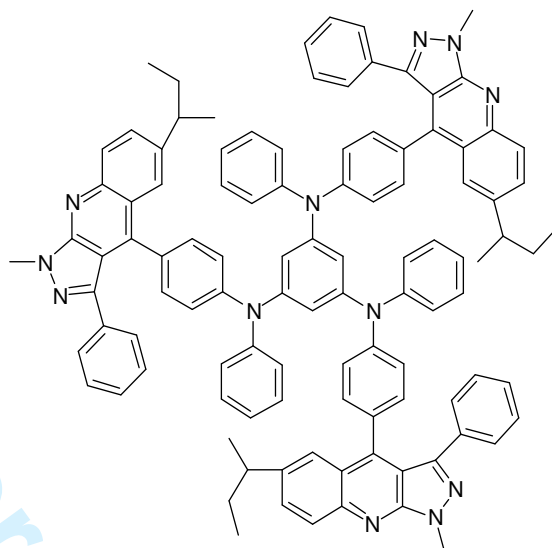


Fig. 1. Optimized geometry structures of the star-burst 1H-pyrazolo[3,4-b]quinoline **3** (SM)

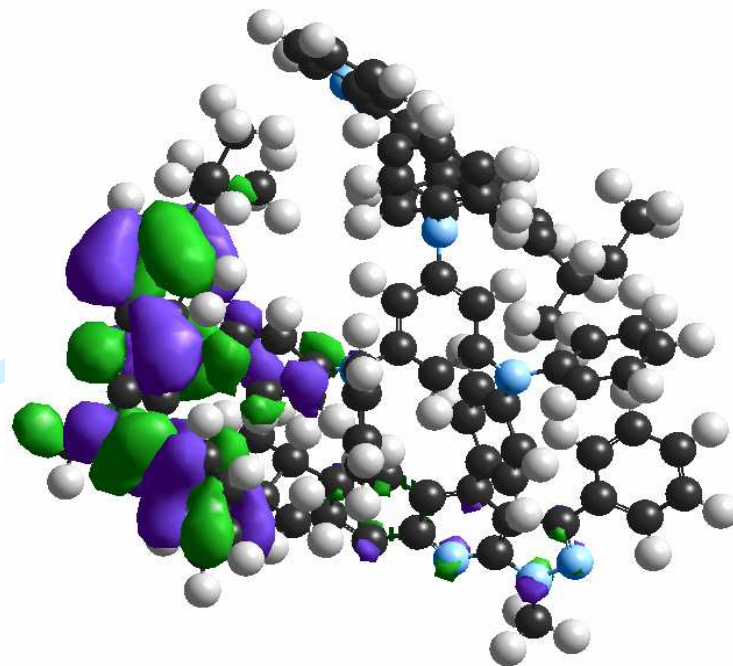


Fig.2. 3D visualization of examined molecules, HOMO levels.

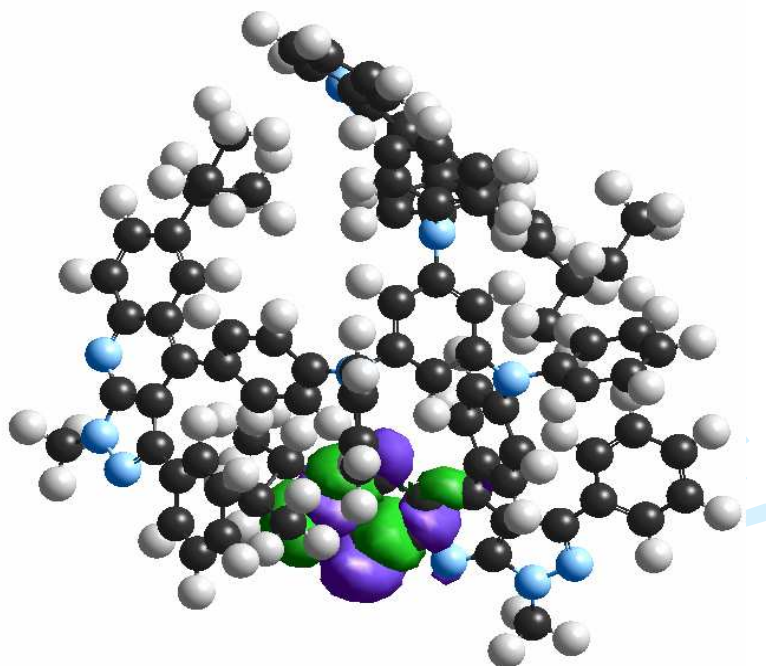


Fig.3. 3D visualization of examined molecules, LUMO levels.

Total ground state dipole moment= 5,6D

4. Results and discussion

4.1 Absorption and photoluminescence

In the Fig. 4 are given the obtained absorbance and photoluminescent (PL) spectra obtained under excitation of the mercury source of the investigated chromophore dissolved in the THF solution for 5 % chromophore solution obtained with spectral resolution 1 nm. One can see a clear Stokes red shift of the PL maximum (at 473 nm) with respect to the absorption maximum at 405 nm. The PL is relatively wide (from 420 nm up to 510 nm), which may indicate on a possible co-existence of several molecular conformations. Additionally the corresponding spectral lines are asymmetric with the red spectral shifts. So one can expect that these chromophore may show emission covering relatively large spectral range. This is particularly crucial for production of LED operating in wide spectral range. The space non-uniformity of the obtained films did not succeeded 1.4 %.

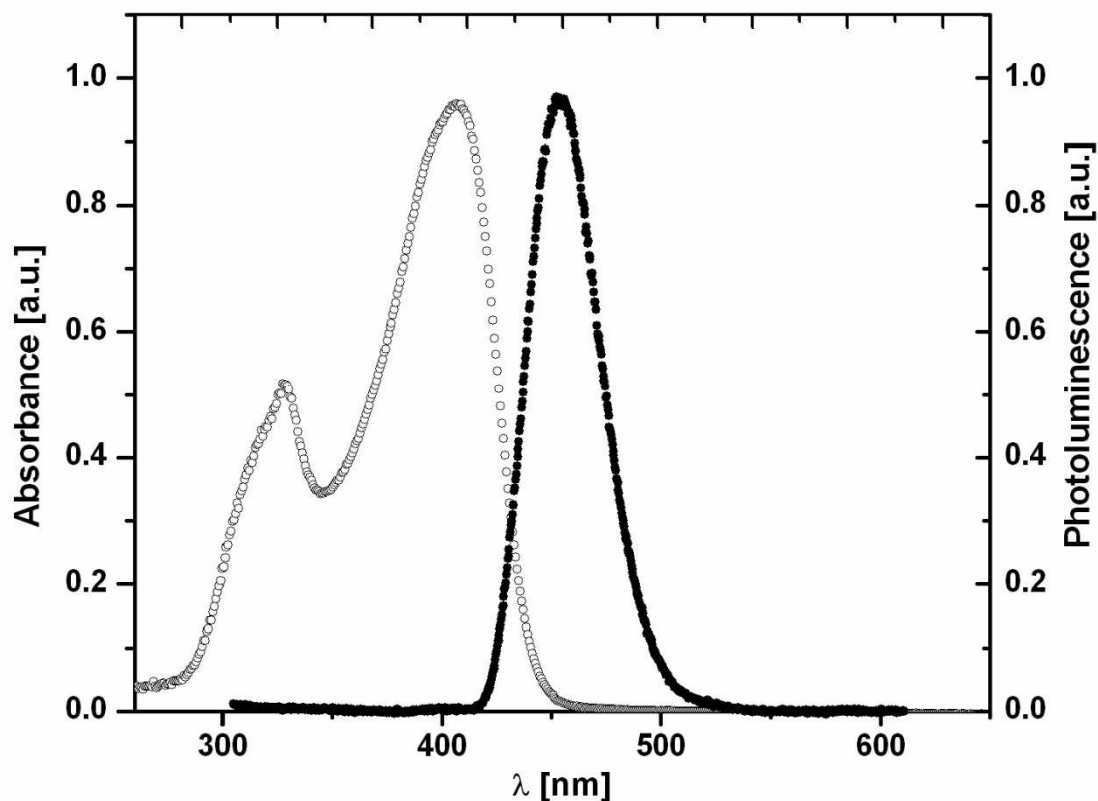


Fig.4. Measured absorption (open circles) and photoluminescent spectra (solid circles) of SM dissolved in THF solution

4.2 Electroluminescent and photovoltaic features.

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4 The EL devices possessing the architecture: indium tin oxide
5 ITO/PEDOT:PSS/PVK+SN/Ca/Al (see Fig. 5A) was fabricated by spin-coating and thermal
6 vacuum deposition technique. The thickness of PEDOT:PSS layer was about 20 nm,
7 PVK+SN – 110 nm, Ca electrode – 10 nm, Al electrode about 100 nm. The non-uniformity of
8 the samples did not exceed 3%. Generally the architecture geometry parameters are similar
9 to the described by us earlier [11]. The organic photovoltaic cells were fabricated by spin
10 coating from the solution onto the glass substrate partially by indium-tin oxide
11 (ITO/PEDOT:PSS/P3OT+SN/Al see Fig 5B).
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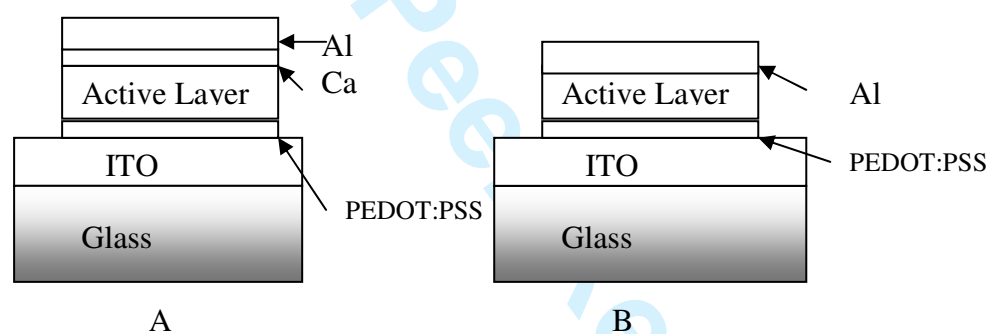


Fig.5. Schemes of single-layer EL (A) and PV(B) devices.

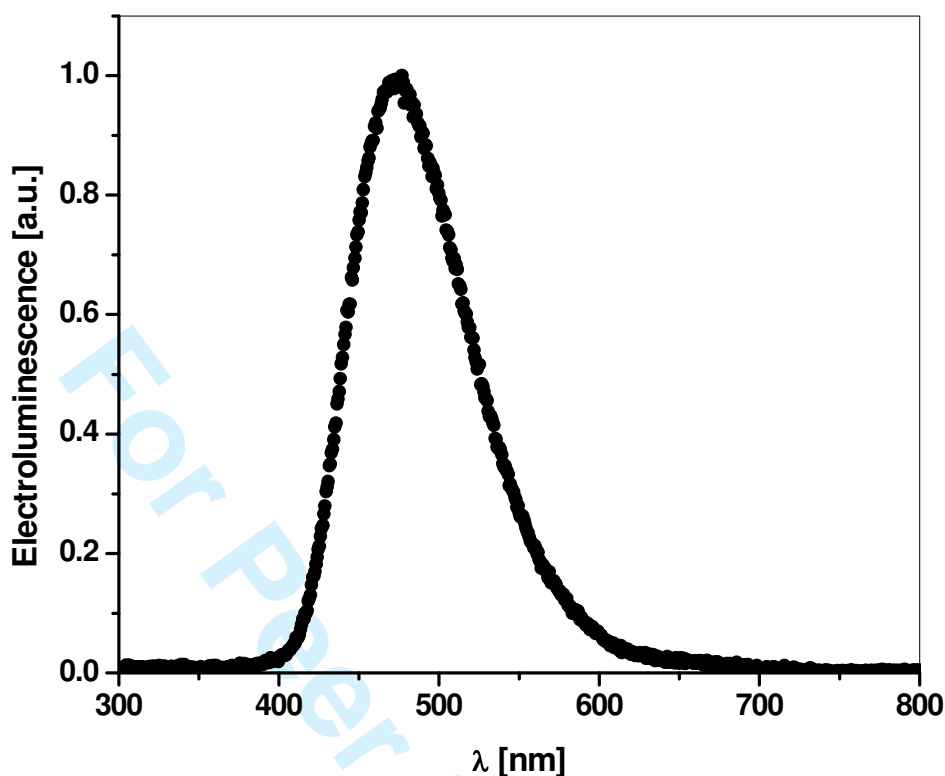


Fig.6. Electroluminescent spectrum of the device based on star-burst PQ

The electroluminescent (EL) spectra obtained for the biased voltage 24 V demonstrate only a slight red spectral shift up to 2 nm with respect to the photoluminescence. So one can expect that the EL is caused by the same molecular levels as the PL. It is principal that the EL spectra are substantially spectrally extended into the red spectral range (about 600 nm) with respect to the PL and cover almost the whole visible range. This is principal difference of the novel synthesized chromophore with respect to the previously investigated [12-14] . This factor may have a huge application potential.

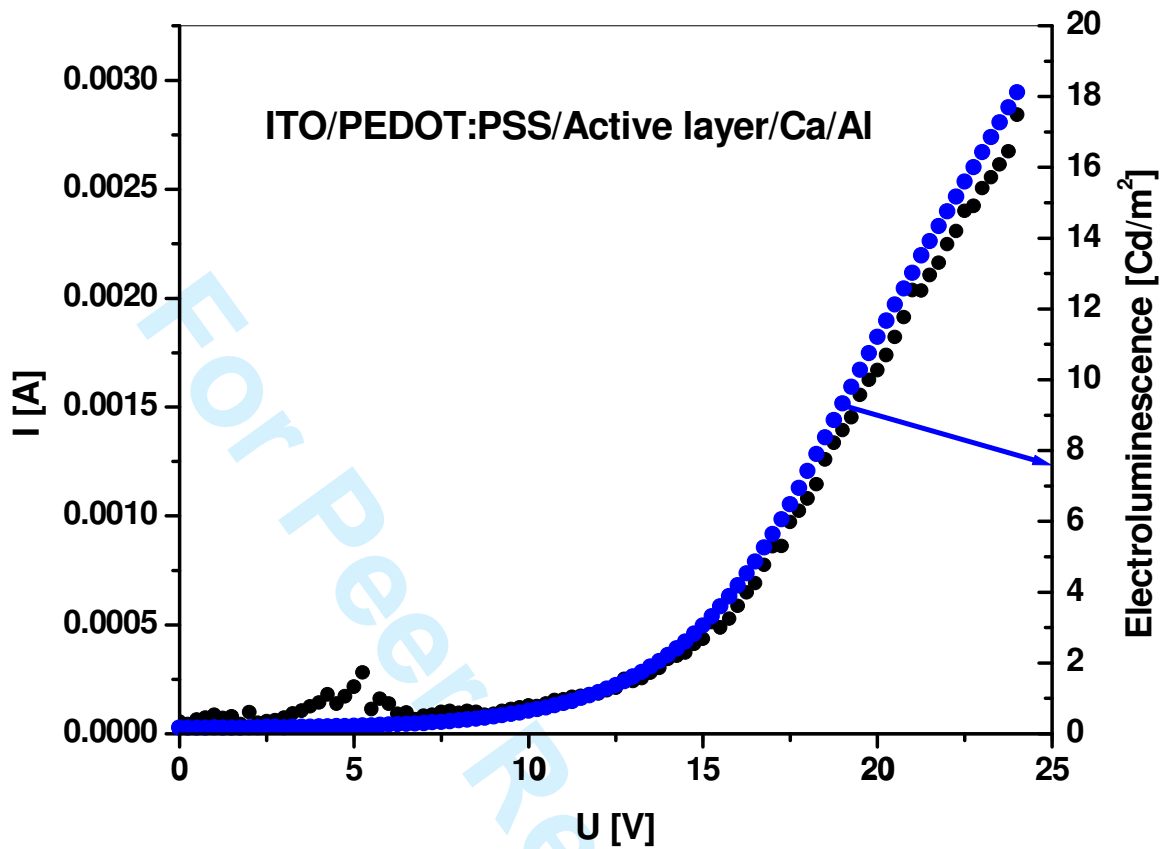


Fig.7. Current-voltage and lumene-voltage dependences for EL device based on star-burst PQ

The principal current-voltage and lumene-voltage dependences are given in the Fig. 7. One can see that the behavior is in a good coincidence. The increase of the EL is occurred at about 10 V achieving maximal derivatives with respect to voltage at about 18 V. A slight peak at about 5 V may indicate on partial depopulation of trapping levels.

We have also studied their PV efficiency, however – it was low 0.8 %, which require additional modifications of the chromophore.

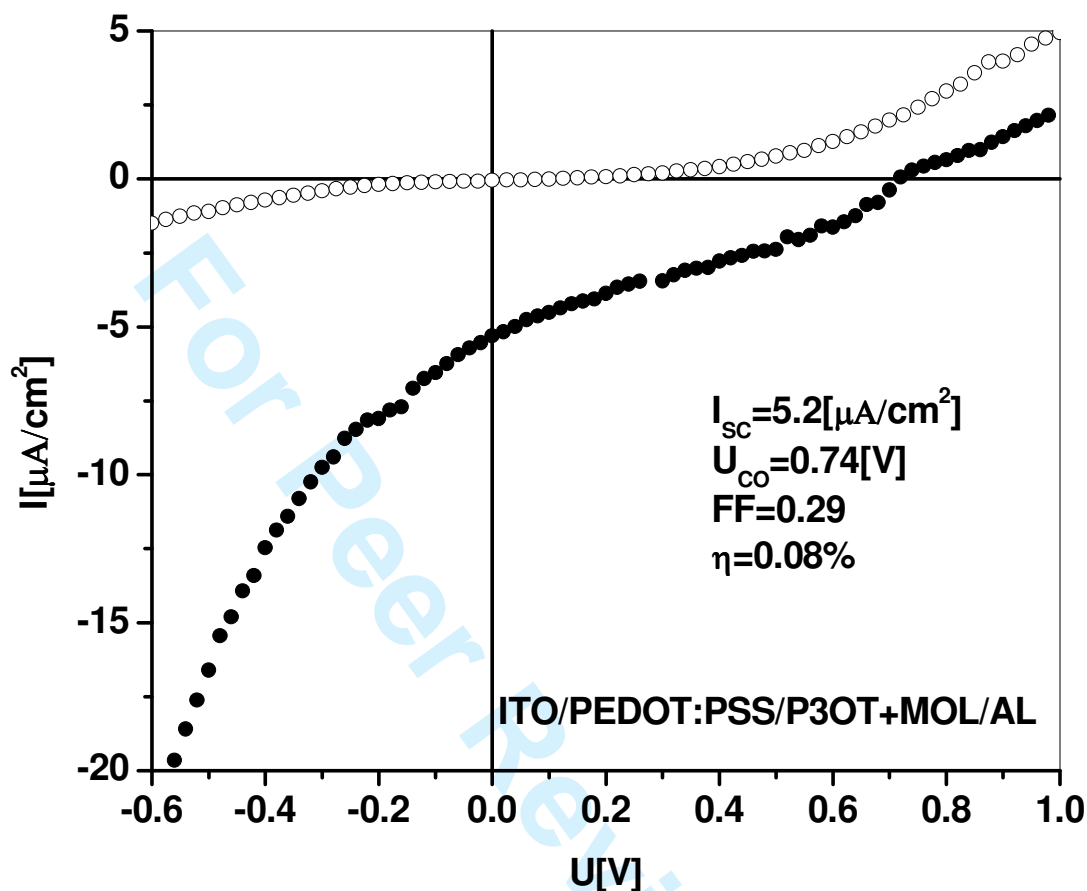


Fig.8. I-V characteristics before (opens rings) and after (black rings) illumination of ITO/PEDOT:PSS/P3OT+MOL / Al devices .

The presented figure clearly show that the present materials possess the photovoltaic response. The relatively low their values (less than 5 D) may indicate on a fact that the dipole-dipole interactions determining the corresponding transport properties and corresponding PV response [15] will be relatively weak. So the main efforts here should be devoted to the alignment of such chromophore during deposition, which may be achieved by appropriate optical treatment [16].

].

Conclusions

The novel star-burst 1*H*-pyrazolo[3,4-*b*]quinoline chromophore were synthesized. The latter may be used for fabrication of LED materials. The LED show substantial spectral extension of emission in the red spectral range. The EL spectra obtained for the biased voltage 24 V

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3 demonstrate only a slight spectral shift up to 2 nm. So one can expect that the EL is caused by
4 the same molecular levels as the PL. It is principal that the EL spectra are substantially
5 spectrally extended into the red spectral range (about 600 nm) with respect to the PL and
6 cover almost the whole visible range. This is principal difference of the novel synthesized
7 chromophore with respect to the previously investigated
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12 13 14 15 16 **Acknowledgments**

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