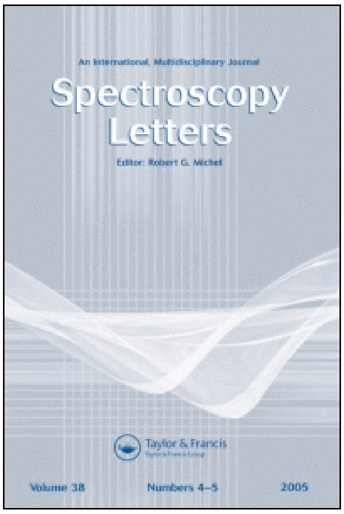

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Spectral Features and Parameters of Some 1*H*-Pyrazolo[3,4-*b*]quinoxaline Derivative Dye Chromophores

E. Gondek[a]; A. Danel[b]; I. V. Kityk[c]; J. Sanetra[a]; J. Niziol[d]
[a] Institute of Physics, Cracow University of Technology, Krakow, Poland [b] Department of Chemistry, University of Agriculture, Krakow, Poland [c] Chemical Department, Silesian Technological University, Gliwice, Poland [d] Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland

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Spectral Features and Parameters of Some 1*H*-Pyrazolo[3,4-*b*]quinoxaline Derivative Dye Chromophores

E. Gondek[1],
A. Danel[2],
I. V. Kityk[3],
J. Sanetra[1],
and J. Niziol[4]
[1]Institute of Physics, Cracow University of Technology, Krakow, Poland
[2]Department of Chemistry, University of Agriculture, Krakow, Poland
[3]Chemical Department, Silesian Technological University, Gliwice, Poland
[4]Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland

ABSTRACT The role of ground state dipole moments of a dye chromophore on the principal features of the light-emitting diodes in the single-layered architecture ITO/PEDOT:PSS/pyrazoloquinoxaline (PQX):PVK/Ca/Al is explored for the first time. The ground state dipole moments of a chromophore determine excitonic carrier kinetics and their annihilation. It was established that the pyrazoloquinoxaline dye chromophores possessing lower dipole moments substantially favor larger electroluminescent efficiency. Parameters of the electroluminescence and current–voltage features are compared with the photoluminescence and absorption characteristics. The UV-Vis spectral absorption, photoluminescence, and current–voltage dependencies indicate a principal possibility to operate by charge kinetics at the almost fixed values of the Highest Occupied Molecular (HOMO) energy levels with respect to the basic ITO hole injector electrodes. Also, a separate role may be played by polaronic effects. We have shown a principal possibility to tune carrier kinetics.

KEYWORDS 1*H*-pyrazolo[3,4-*b*]quinoxaline derivatives, organic light emitting diodes

INTRODUCTION

In recent years, organic light-emitting diodes (LEDs) have received much attention due to their potential application in flat-panel displays. The materials that are applied in this area can be divided into small molecules, oligomers, and polymers. Each class has their own advantages and drawbacks. Very often, these materials may serve simultaneously as photovoltaic cells. The heterocyclic compounds can be found in each class. The nitrogen heterocycles are one of the most important ones. For example, AlQ_3 was employed by Tang and Vanslyke as electron-transporting material in a two-layer device.[1] Since that time, many quinoline derivatives were applied as efficient electron transporting and emissive materials. Earlier, we fabricated some electroluminescent devices (vacuum evaporated, polymer or PVK doped) based on new luminophores belonging to the class of 1*H*-pyrazolo[3,4-*b*]quinoline.[2–4] This system is relatively old as the first

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Address correspondence to E. Gondek, Institute of Physics, Cracow University of Technology, Podchorazych 1, 30-084, Krakow, Poland. E-mail: e.gondek@wp.pl

examples were prepared in 1928 by Tomasik et al.[5] Since that time, these compounds were explored prevailingly as biologically active compounds. Due to very high quantum efficiency, we have decided to use them in electroluminescent devices. In some cases, a maximum luminance of 37,000 cd/m^2 was obtained at 10.0 V, and the maximum power, luminance, and external quantum efficiencies were obtained to be 4.2 lm/W, 6.0 cd/A, and 1.6%, respectively, at 5.0 V.[2] The device with configuration ITO/PEDOT/PVK:PQ/CsF/CaMg emitted blue light with CIE$_{x,y}$ coordinates (0.15; 0.07).[3] These parameters as far as CIE$_{x,y}$ are comparable with the excellent devices based on anthracene derivatives.[6] Quinoline derivatives exhibit promising electron-transporting properties, which may be used simultaneously in the light-emitting diodes and photovoltaic cells. The same properties can be found among quinoxaline derivatives, too.

The higher electron affinity in the comparison with quinoline is connected with the presence of additional nitrogen atom in the benzene ring. Strohriegl applied bis(phenylquinoxaline) and starburst tris(phenylquinoxaline) as electron-transporting materials for LEDs.[7,8]

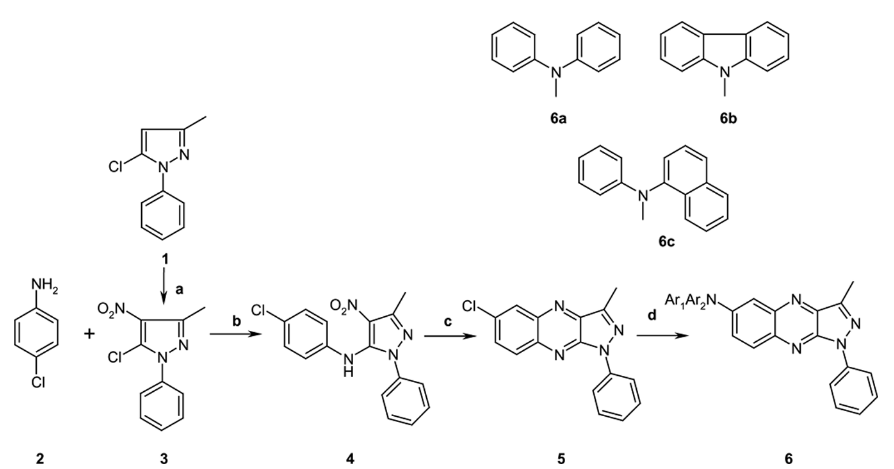
Just recently, Lee published the results on application of some 1*H*-pyrazolo[3,4-*b*]quinoxalines (PQX) as materials for OLEDs. Green emitting electroluminescent devices were fabricated using these compounds as dopants in AlQ$_3$ matrix in the device with configuration ITO/NPB/AlQ$_3$:PQX/AlQ$_3$/MgAg. This was the first case of application of PQX in electroluminescent devices.

In this work, we report the synthesis and electroluminescent properties of some 1*H*-pyrazolo[3, 4-*b*]quinoxalines substituted with 6-*N,N*-diaryl substituents and explore their features as LED materials. We will study UV-Vis absorption and photoluminescence in the solution. After, we explore their electroluminescence and current–voltage dependencies for the/PEDOT:PSS/pyrazoloquinoxaline PQX:PVK/Ca/Al LED architecture. We will additionally perterm quantum chemical calculations to explore the role of the dipole moments in the observed dependencies.

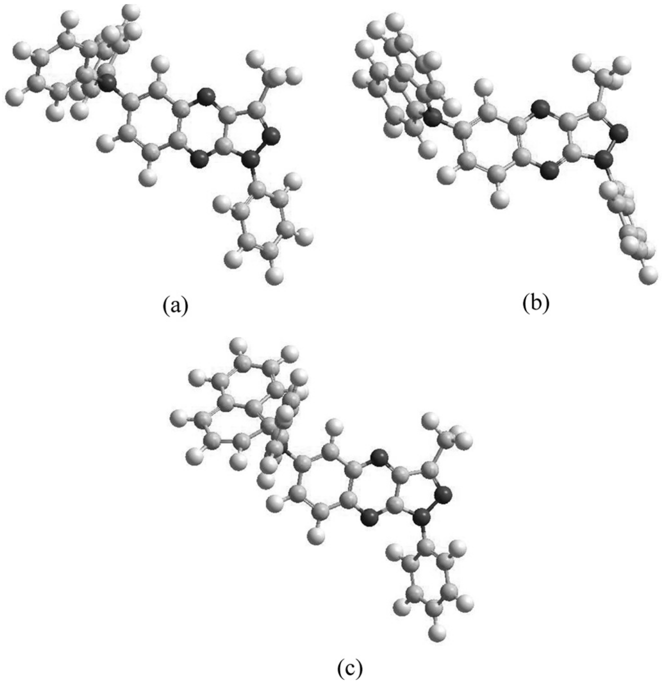
MATERIALS AND METHODS

Chromophore Synthesis

The synthetic procedure for 1*H*-pyrazolo[3, 4-*b*]quinoxalines is depicted in Scheme 1. Thus, commercially available 5-methyl-2-phenyl-2,4-dihydropyrazol-3-one was chlorinated with POCl$_3$ yielding 5-chloro-3-methyl-1-phenylpyrazole **1** and next transformed into nitro derivative **2**. 5-Chloro-3-methyl-4-nitro-1-phenylpyrazole **3** was reacted with *p*-chloroaniline **2** in DMF in the presence of anhydrous K$_2$CO$_3$. 6-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline **6** was prepared by cyclization of **4** with triethyl phosphite.[9] Chloro derivative **6** was aminated with *N,N*-diphenylamine, carbazole, and *N*-phenyl-1-naphthylamine in the presence of 2-dicyclohexylphosphino-2′,4’,6′-triisopropylbiphenyl and Pd(Ac)$_2$ yielding **6a**, **6b**, and **6c** respectively (Fig. 1). In the past study, we



SCHEME 1 (a) Fuming HNO$_3$/(CH$_3$CO)$_2$O, −10°C; (b) K$_2$CO$_3$/DMF/130°C; (c) P(OEt)$_3$/160°C; (d) Pd(OAc)$_2$/phosphine ligand/Cs$_2$CO$_3$/PhMe/*tert*-BuOH(5/1)/90–110°C.


(a) (b)

(c)

FIGURE 1 Chemical formulas of the investigated pyrazoloquinoxaline dye molecules.

prepared these compounds with a different catalytic system based on (*o*-biphenyl)P(*tert*-Bu)$_2$/Pd(OAc)$_2$. The yields of **6a**, **6b**, **6c** are similar in both cases, and an improvement in the yield was not observed.[10] There are some alternative methods of amination with copper catalysts instead of palladium ones. In this case, the attempt of amination with this type of catalyst failed. The chloro derivatives **5** were unreactive. The same procedure applied to bromo derivatives gave good results but the yield of the synthesis of 5-bromo-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline was very low (5–6%) so the reaction has no practical application.

(4-Chlorophenyl)-(5-methyl-4-nitro-2-phenyl-2*H*-pyrazol-3-Yl)amine (4)

Equimolar amounts (0.02 mol) of aniline **2** (2.54 g) and **3** (4,74 g) were heated in NMP (15 mL) with K_2CO_3 (2.80 g, 0.02 mol) for 6 h at 130°C. After cooling, the reaction mixture was poured into ice/water mixture, neutralized with 10% HCl, and stirred for 2 hours. The precipitate was filtered off, dried, dissolved in $CHCl_3$, and filtered through a short column packed with aluminum oxide.

Yellow crystals, 51%, m.p. 172–173°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.66$ (s, NH); 7.26–717 (m, 7H); 6.96 (d, $J = 8.7$ Hz, 2H); 6.69 (d, $J = 8.7$ Hz, 2H); 2.6 (s, 3H). Analysis: Calcd. for $C_{16}H_{13}ClN_4O_2$: C, 58.46; H, 3.99; N, 17.04. Found: C, 58.33; H, 3.16; N, 16.91.

6-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (5)

Nitropyrazole **4** (0.005 mol, 1.6 g) and triethyl phosphite (7.5 mL) was heated under reflux for 24 h in an inert atmosphere. The excess of triethyl phosphite was distilled off, and the product was purified by column chromatography (10–30% EtOAc in toluene).

Yellow crystals, 43%, m.p. 193–195°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.44$ (d, $J = 8.8$ Hz, 2H, 2,6-H_{1Ph}); 8.30 (d, $J = 1.9$ Hz, 1H, 5-H); 8.17 (d, $J = 9.1$ Hz, 1H, 8-H); 7.80 (dd, $J = 9.2$ Hz; 2.3 Hz, 1H, 7-H); 7.60 (t, $J = 7.9$ Hz, 2H, 3,5-H_{1Ph}); 7.33 (t, $J = 7.4$ Hz, 1H, 4-H_{1Ph}). Analysis: Calcd. for $C_{16}H_{11}ClN_4$: C, 65.20; H, 3.76; N, 19.01. Found: C, 65.28; H, 3.85; N, 18.76.

1*H*-Pyrazolo[3,4-*b*]quinoxalines (6: general procedure)

An oven-dried (150°C) 20-mL round-bottom flask equipped with a Teflon-coated magnetic stir bar and reflux condenser was charged with 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (11.9 mg, 0.0250 mmol), Pd(OAc)$_2$ (2.3 mg), reactants (0.5 mmol of **5** and 0.75 mmol of amine) and Cs_2CO_3. The flask was closed with rubber septum, evacuated, and backfilled with nitrogen. Solvent deaerated with argon (toluene/*tert*-BuOH), 10 mL, was added through the septum via syringe. The flask was heated on an oil bath at 110°C for 48 h. The reaction mixture was allowed to cool down to room temperature and filtered through a filtering stick and evaporated.

The resulting compounds were purified on preparative TLC plates (Merck, silica-gel, 2 mm).

(3-Methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxalin-6-yl)-diphenylamine (6a)

Orange powder, 45%, m.p. 212–213°C, lit. 212–213°C.[10]

6-(Carbazol-9-yl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoxaline (6b)

Yellow powder, 51%, m.p. 180–181°C, lit. 180–181°C.[10]

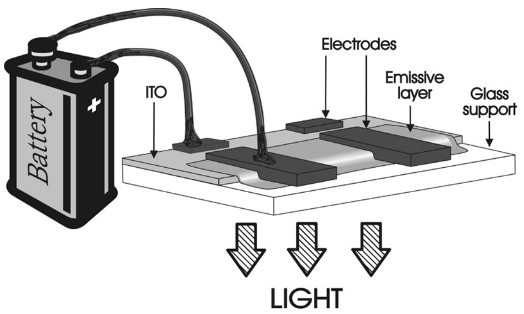


FIGURE 2 Schematic illustration depicting the general structure of a single-layer LED device used in the reported work.

(3-Methyl-1-phenyl-1H-pyrazolo[3,4-b]quinoxalin-6-yl)-naphtalen-1-yl-phenylamine (6c)

Orange powder, 55%, m.p. 212–213°C, lit. 212–213°C.[10]

LED Preparation

The titled LED with a single-layer structure (Fig. 2) was fabricated in the following manner. Substrate glass slides pre-coated with transparent ITO (conductive transparent indium–tin oxide, sheet resistance of $20\,\Omega/\mathrm{sq}$) were ultrasonically cleaned in detergent solution, followed by thorough rinsing in deionized water. They were then cleaned in chloroform, dried in vacuum at 100°C during 30 min, and cooled to ambient temperature. In the next step, the substrates were covered by spin-coating technique with intermediate layer of PEDOT:PSS (poly[3,4-ethylenedioxythiophene] poly[styrenesulfonate]) latex and again put in vacuum drier at 100°C for 30 min to remove residues of water. The studied chromophore and PVK (poly[*N*-vinylcarbazole]) were dissolved in chloroform, a common solvent for both. Prior to deposition, the solution was bubbled with dried argon to remove dissolved air. The solution was deposited on the substrate through spin-coating technique at 1000 RPM. The sample was kept at 70°C for 60 min to remove surface strains appearing as a result of rapid solvent evaporation during the spinning.

Finally, electrodes were deposited by vacuum evaporation through resistive heating. They consisted of 10 nm of Ca covered with 100 nm of Al.

RESULTS AND DISCUSSION

UV-Vis absorption and photoluminescence (PL) spectra were measured in tetrahydrofuran solution using an Oriel Instaspec II monochromator/diode array detector for 5% solvent solution. Solution spectrophotometric measurements were performed using standard 1-cm pathlength quartz crucible for absorption and luminescence spectrometry with 1-nm spectral resolution. The luminescent spectra were recorded for mercury lamp.

Typical electroluminescence (EL) spectra of the so-prepared LED are presented in Fig. 3. One can see that the spectral maxima for **6b** containing LED are spectrally shifted to lower wavelengths (up to 520 nm) with respect to the two other chromophores situated at 570–580 nm. All the curves demonstrate spectral asymmetry of the EL spectra with considerable broadening to the red wavelengths. This is typical for these compounds. The reasons are because of existence of several chromophore conformations and existence of the electron-vibration replica closely related to the polaronic effects.

Additional asymmetry of the obtained PL spectra may indicate a substantial role of the low-energy polaronic states effectively changing the absorption cross section. All the PL spectra demonstrate almost the mirror-like Stokes shift with respect to the absorption spectra. The Stokes red shift is varied from 70 nm up to 120 nm.

The EL spectra presented in Fig. 4 unambiguously demonstrate that the spectral positions for the three principal EL peaks are in a good accordance with such positions for the PL (Fig. 3). Moreover, an

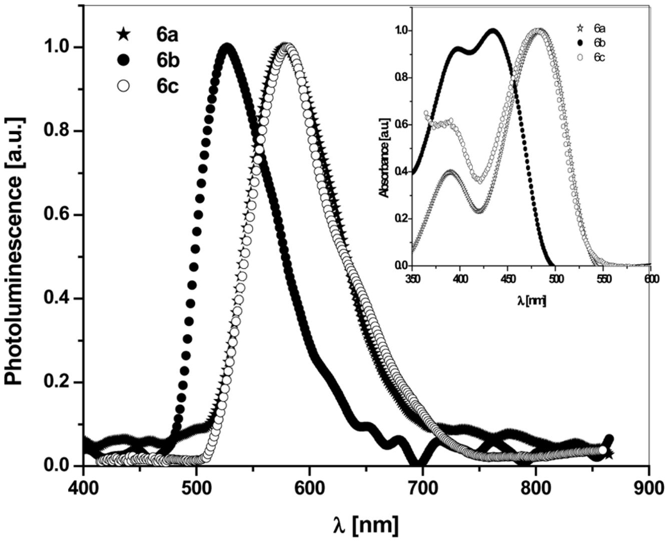


FIGURE 3 PL spectra of the investigated chromophores in THF solution. In the insert is given the absorption spectra.[10]

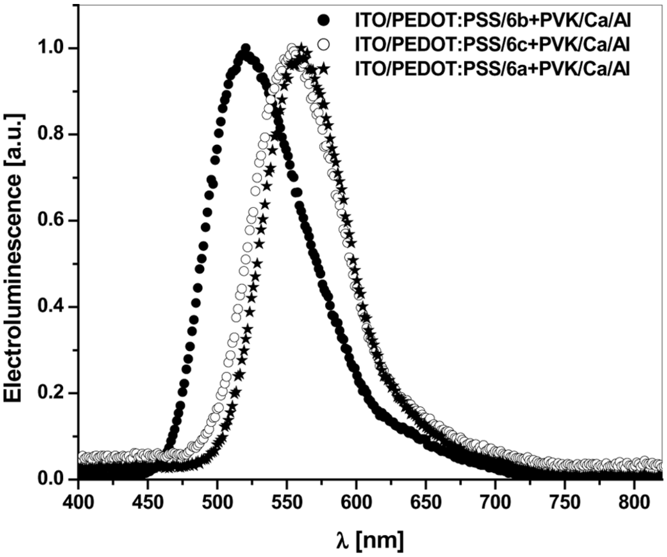


FIGURE 4 Typical spectral dependencies of the EL spectra for the titled LED geometry obtained during excitation by the mercury lamp and at 10 V.

existence of tails at about 620 nm may indicate an existence of the polaronic states determining the trapping of the free carriers during application of external dc electric field. In this case, the interconformational Boltzmann distribution will be suppressed under ordering of the external field. Following the additional asymmetry of the EL spectra with respect to the PL spectra, one can assume that the ground state dipole moments may play a dominant role in this case.

To explore this influence, we have performed quantum chemical calculations of the investigated chromophore within the framework of the B3LYP method. The corresponding parameters are given in Table 1.

Following the data presented in the Table 1 with respect to the ground state dipole moment values and comparing them with the results presented in Figs. 3–6, one can find a striking correlation of the ground state dipole moments with the principal spectral features of the investigated chromophores.

TABLE 1 Principal Quantum Chemical Parameters of the Investigated Chromophores

Molecule	EL$_{max}$ (nm)	PL$_{max}$ (nm)	M (D)
6a	559	576	2.32
6b	520	527	4.02
6c	554	570	2.08

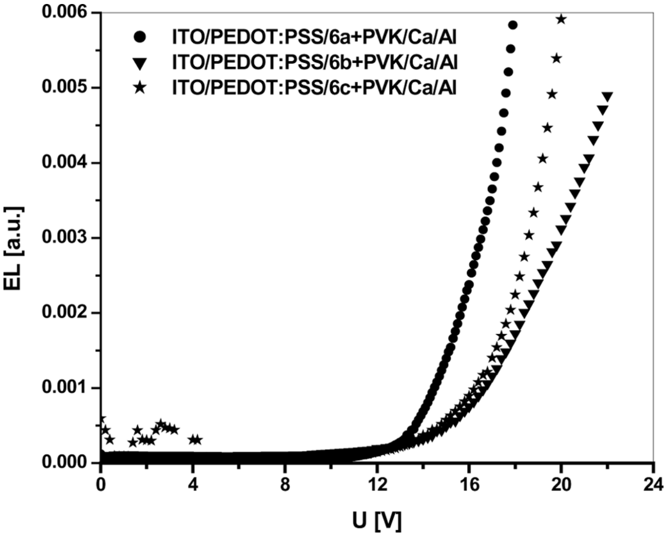


FIGURE 5 Electroluminescent dependencies for the luminophores.

It should be emphasized that the value of the ground state dipole moment for **6b** containing LED is almost two times larger with respect to the two other dyes. This may explain the lower EL efficiency for the **6b** LED. The physical origin of the observed phenomenon is based on the dipole–dipole interactions between the titled chromophore and the polymer chains. The higher dipole moments favor formation of the more stable (energetically deeper) excitons. Thus to achieve their annihilation creating the desired EL spectrum, we need to apply the larger dc electric field. The current–voltage dependencies clearly confirm this assumption.

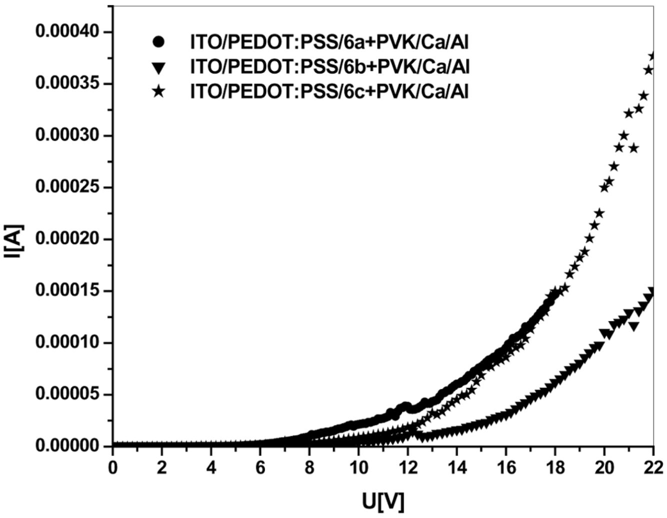


FIGURE 6 Current–voltage dependencies for the three luminophores.

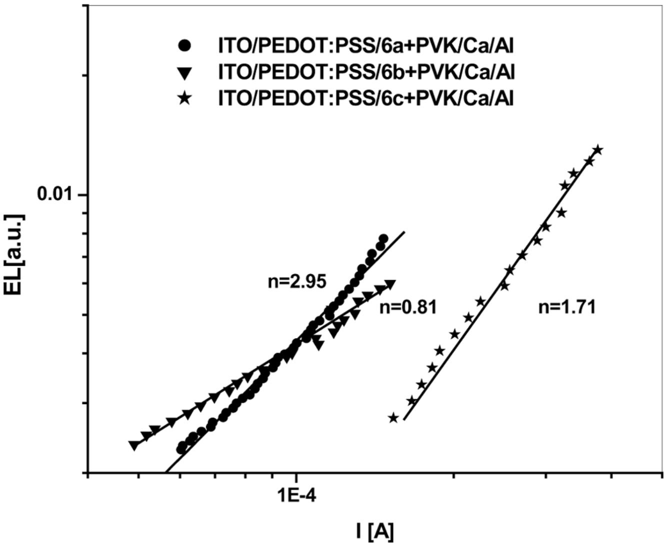


FIGURE 7 EL-current dependencies of the EL spectra.

Following this reason, the physical mechanism for the **6b** sdye chromophore should be substantially different. From Fig. 7 one can see that the power current–dependent coefficient for the **6b** LED is substantially different than for the other two dyes. This situation opens a rare opportunity to operate by the emission properties of the investigated LED using the active chromophore with different ground state dipole moments. This is impossible for the fluorescent materials based on the rare earths or transition metal activators.[11]

CONCLUSIONS

We have explored electroluminescent and current–voltage dependencies for the/PEDOT:PSS/ pyrazoloquinoxaline PQX + PVK/Ca/Al LED architecture. Following the quantum chemical calculations of the ground state dipole moment values and comparing them with the experimental results concerning the absorption, photoluminescence, electroluminescence, and current–voltage dependencies, we have found a striking correlation of the ground state dipole moments with the principal spectral features of the investigated chromophores. It should be emphasized that the value of the ground state dipole moment for the molecule **6b** containing LED is almost two times larger with respect to that of the two other dyes. This may explain the lower EL efficiency for the **6b** LED with respect to the other ones. The physical origin of the observed phenomenon is based on the dipole–dipole interactions between the titled chromophore and the polymer chains. The higher dipole moments favor formation of the more stable (energetically deeper) excitons. The principal role here is played by polaronic states associated with trapping levels.

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