Advanced Device Materials

Original Research Paper

Solution processable double layer organic light emitting diodes (OLEDs) based on 6-*N,N*-arylsubstituted-1*H*-pyrazolo[3,4-*b*]quinolines

Andrzej Danel[1], Łukasz Chacaga[1], Tomasz Uchacz[2], Monika Pokladko-Kowar[3], Ewa Gondek[3], Paweł Karasiński[4] and Bouchta Sahraoui*[5]

[1]Institute of Physics and Chemistry, The H. Kołłątaj University of Agriculture, ul. Balicka 122, 31-149 Krakow, Poland
[2]Department of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, Poland
[3]Institute of Physics, Cracow University of Technology, Podchorazych 1, 30-084 Krakow, Poland
[4]Department of Optoelectronics, Silesian University of Technology, ul. Krzywoustego 2, 44-100 Gliwice, Poland
[5]LUNAM Université, Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 2 bd Lavoisier, 49045 Angers Cedex, France

Abstract Three 1*H*-pyrazolo[3,4-*b*]quinolines (PQs) with *N,N*-diarylamine moiety were synthesized. They were used as dopants in poly(9-*N*-vinylcarbazole) (PVK) matrice. An additional star burst oligoquinoline TRI-Q electron transporting layer was deposited on emission layer from solution. The devices with configuration ITO/PEDOT:PSS/PVK-PQ/TRI-Q/Ca/Al show bright green emission with luminance $L = 355–806$ cd m^{-2}.

Keywords Organics compounds, Thin film, OLED, Green emission
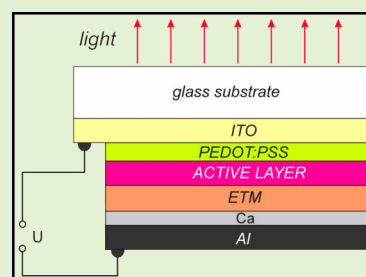
Introduction

At present, organic materials are widely used in the fabrication of electronic devices. The most important ones include organic light emitting diodes (OLEDs), organic photovoltaic devices and organic effect field transistors.[1–6] For the first time, the electroluminescence phenomenon based on anthracene crystals was demonstrated in 1963 by Pope *et al*.[7] Those days such organic devices could not compete with commercially available light emitting devices based on inorganic emitters, such as gallium arsenide phosphide. One of the obstacles was the high driving voltage and the technological fabrication problems. The breakthrough occurred in 1987 when Tang and VanSlyke fabricated multilayer OLED based on small organic molecules. In very short time, OLED based on polymers were invented by Friend and Heeger's independently.[8,9] Currently, organic light emitting devices are widely employed in cell phones, digital cameras and white light emitting panels. These devices can be fabricated either by vacuum evaporation of small molecules or by spin cast polymer layers. The first

method allows constructing devices with finely tuned layers so as to match the migrating holes and electron in emitting layer where the opposite charges recombine forming exciton with subsequent light emission based on fluorescence or phosphorescence phenomenon. However, there is one serious drawback of this technique, namely, the loss of materials up to ~70%.[10] This negative factor can be avoided if organic material can be spin cast or ink jet printed from appropriate solvent forming a single layer of electron transporting materials (ETMs), hole transporting materials (HTMs) or light emitting material. Heeger applied this method in the case of a solution processable polymer based device with configuration ITO/PEDOT/MEH-PPV/Al. The device emitted orange red light with luminance $L_{max} = 220$ cd m^{-2} at 3.8 V.[9] Besides poly-*para*-phenylene vinylene type polymers (PPV), many other ones such as polyfluorenes, polythiophenes or poly(*N*-heterocycles) were used in fabrication of single layer devices from solutions.[11–13] However, these devices usually exhibit lower performance in the comparison with electroluminescence cells fabricated with dry techniques. In part, it is connected with the fact that it is very difficult to find solution processable material with well balanced hole–electron mobility serving simultaneously as light emitter. This problem can be solved by spin casting a mixture of hole

---

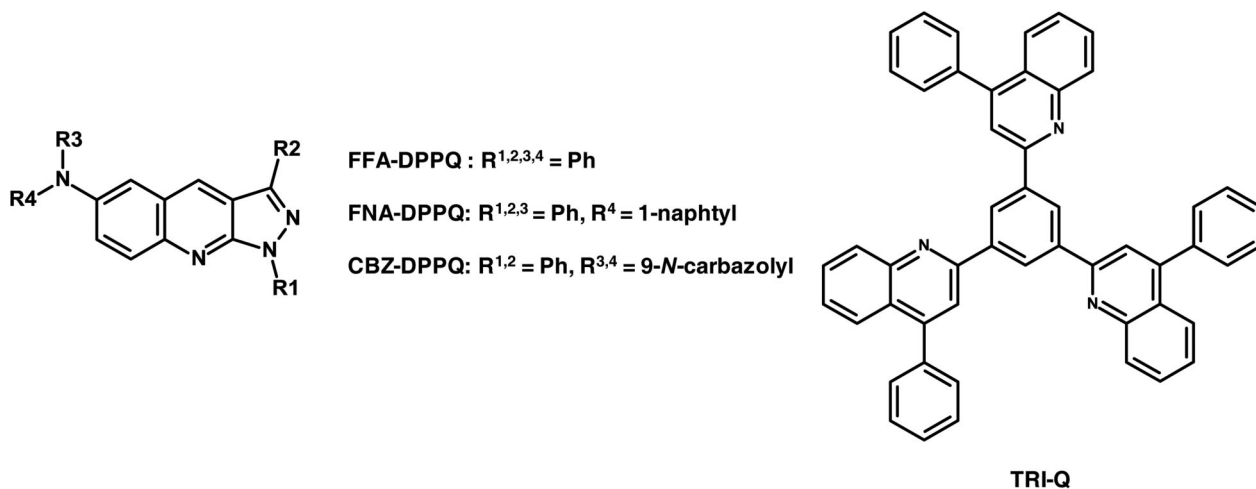*Corresponding author, email bouchta.sahraoui@univ-angers.fr

Figure 1   Molecular structures of pyrazoloquinoline (DPPQ) based luminophores and electron transporting material TRI-Q

transporting material such as poly(9-*N*-vinylcarbazole) (PVK) or 4,4′-bis(*N*-carbazolyl)biphenyl with emitter (fluorescent or phosphorescent) and electron transporter like 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) or oxadiazole derivatives.[14–16] Just recently, new solution processable small molecules serving as HTM, ETM or emissive materials have been introduced. Many of them are based on *spiro*, *cardo* or *tetrahedral* molecular geometry concept and can be easily processed forming amorphous pinehole free films.[17–20] But the real challenge for OLED industry is fabrication of multilayer devices with wet techniques such as spin coating, doctor blade, ink jet printing or roll to roll process. The main obstacle is dissolution of dry cast layer with the subsequent solution. This can be avoided by creating insoluble layer of organic materials. Holmes *et al.* fabricated two layer device with configuration ITO/PPV/DP-PPV/Ca.[21] The insoluble PPV layer was formed first via Wessling–Zimmermann route (thermoconversion method) and next a solution of poly(2,3-butyloxy-1,4-phenylene vinylene) (DP-PPV) was spun coated from tetrachloroethane solution. Jenekhe and Alam tested various polybenzobisazoles as electron transporting materials with PPV combination. The ETMs were cast from methanesulfonic acid solution on PPV layer.[22] The solvent resistant polymer layer can be also formed from photo- or thermocross-linkable precursors.[23–25] Another approach of fabricating of multilayer OLED is the application of orthogonal solvents which would not dissolve the underlying hole transporting or emissive layer. Jenekhe *et al.* synthesized a group of star shaped oligoquinolines with electron transport properties. Two layer phosphorescent OLED with configuration of ITO/PEDOT:PSS/PVK-FIrpic-OXD-7/oligoquinoline/Al were constructed. The ETM layer was either evaporated or spin cast from formic acid solution which does not dissolve PVK polymer blend.[26] He applied also various commercially available derivatives of phenantroline as solution processable ETMs.[27,28] Just recently, Duan *et al.* reported a paper describing a fully solution processed electrophosphorescent device. The emission layer was a host–guest mixture of phosphorescent emitter FIrpic, electron transporting oxadiazole based material OXD-7 and carbazole derivative Cz-TCB as hole transporter HTM. It was spin coated from 1,2-dichloroethane solution with

subsequent casting of isopropanol soluble tris(4-(diphenyl-phosphoryl)phenyl)benzene as ETM.[29]

In the present work, we demonstrate the synthesis and electroluminescent properties of some 6-*N*,*N*-diarylsubstituted 1*H*-pyrazolo[3,4-*b*]quinolines applied as emitters in two-layer solution processable OLED (Fig. 1). 1*H*-Pyrazolo-[3,4-*b*]quinolines (PQs) are compounds with strong emissive properties predominantly in blue and green. In spite of the fact that the first compounds of this class were synthesized at the beginning of twentieth century, little was known about their photophysical properties. The first investigations were undertaken by Rotkiewicz *et al* in the late 90s of twentieth century.[30] Unsubstituted PQs show a fluorescence quantum yield equal to unity, independent of solvent. They exhibit strong luminescence in the solid state as well. That is why we chosen them as luminophores for OLED. The first PQ based OLED were multilayer devices.[31,32] The other ones were single layer electroluminescent cells in which PVK served as hole transporting material for doped PQs.[33]

Experimental

Materials

All starting materials used for synthesis were purchased from commercial suppliers such as Aldrich and Fluka. All solvents for chromatography were purchased from Polish chemical supplier POCh. ^{1}H NMR and ^{13}C NMR were recorded on spectrometers operating at 600 and 150 MHz respectively in CDCl₃. Chemical shifts are reported in ppm from tetramethylsilane as an internal standard. The progress of reactions was monitored with TLC plates covered with silica gel (0.25 mm) and visualized with UV light (254 and 364 nm). Melting points were determined with Melt-TEMP apparatus (Aldrich) and are uncorrected. Tris(dibenzylidene)palladium was prepared according to literature procedure.[34]

Synthesis

5-chloro-1,3-diphenylpyrazole-4-carbaldehyde 1

To a two neck, round bottom flask (25 mL) equipped with magnetic stirring bar, thermometer and reflux condenser was added dimethylformamide (2.5 mL). The flask was immersed in ice/NaCl mixture and POCl₃ (7.1 mL) was added in portions maintain the temperature below −10°C. After

finishing addition of $POCl_3$ the mixture was allowed to warm to room temperature and 2,5-diphenyl-4*H*-pyrazol-3-one (2.6 g, 0.01 mol) was added in one portion. The contents were stirred at room temperature for 20 min and the flask was immersed in the preheated oil bath and heated for 3 h at 120°C. After cooling the mixture was poured into ice/water mixture, neutralized with 10% NaOH and stirred for a night. The precipitate was filtered off, dried, dissolved in chloroform and filtered through a pad of aluminum oxide. The solvent was removed to give colorless crystals, 2.6 g, 86%, mp. 105–106°C lit.[35] 107–108.5°C.

6-Bromo-1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline 3a

In the round-bottomed flask (20 mL) a mixture of *p*-bromoaniline (2.1 g, 0.012 mol) and pyrazole **1** (2.8 g, 0.010 mol) was placed and heated within 120–180°C. The heating was continued up to the cease of HCl evolution (indicator paper). After the cooling, the reaction mixture was dissolved in $CHCl_3$, filtered and purified on column packed with aluminum oxide using $CHCl_3$ as eluent. Yellow crystals, 3.5 g, 87%, mp. 189–191°C (toluene)

^{1}H NMR (600 MHz, $CDCl_3$): 8.77 (s, 1H), 8.56–8.55 (m, 2H), 8.14 (d, $J=2,2$ Hz, 1H), 8.12–8.10 (m, 2H), 8.03 (d, $J=9.1$ Hz, 1H), 7,.81 (dd, $J=9.1$ Hz, 2.2Hz, 1H), 7.61–7.56 (m, 4H), 7.52–7.50 (m, 1H), 7.34–7.14 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 150.8; 146.6; 144.5, 139.7, 134.2, 132.3, 130.8, 130.6, 129.9, 129.2, 129.1, 129.0, 127.5, 125.7, 125.6, 120.7, 117.8, 116.9.

Analysis calculated for $C_{22}H_{14}BrN_3$: 66.02C–3.35H–10.49N. Found 65.89C–3.29H–10.34N.

p-(N-1,N-1)-diphenyl)-phenylenediamine 5a

Compound was synthesized according to literature procedure[36]

N-(4-Aminophenyl)-N-phenyl-1-naphtylamine 5b

Compound was prepared according to literature procedure [37]

4-(9-Carbazolyl)aniline 5c

Compound was synthesized according to literature procedure[38]

N,N,1,3-Tetraphenyl-1H-pyrazolo[3,4-b]quinoline (FFA-DPPQ): general procedure

Method A

A mixture of 6-bromo-1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline (1.25 mmol, 500 mg), diphenylamine (1.50 mmol, 250 mg), bis(dibenzylideneacetone) palladium(0) (2.5 mol.-%, 29 mg), (2-biphenylyl)di-*tert*-butylphosphine (1 mol-%, 2.9 mg), sodium *tert*-butoxide (2 mmol, 200 mg) and toluene (5 mL) were loaded into the tube and flushed with argon. The tube was immersed into a preheated oil bath (100°C) for 24 h. After completion of a reaction as judged by TLC analysis, the reaction mixture was diluted with EtOAc and filtered. The filtrate was concentrated under reduced pressure yielding oil. The crude product was purified on column packed with aluminum oxide using toluene as eluent. To prepare an analytical sample of FFA-DPPQ, the final purification was accomplished with preparative thin layer chromatography (Merck plates 20 × 20 cm, covered with silica gel, 2 mm) using toluene/petrol ether (3:1) as eluent. The same purification procedures were applied for FNA- and CBZ-DPPQs. Yellow crystals, 350 mg, 71%, mp. 232°C (toluene). Lit.[31] 232–234°C.

Method B

A mixture of 5-chloro-1,3-diphenylpyrazole-4-carbaldehyde **1** (1 mmol, 280 mg) and *p*-(N,N-diphenyl)phenylenediamine **5a** ($Ar^{1,2}$=Ph) (1.2 mmol, 320 mg) were heated in a small flask on oil bath within the range 140–200°C. When the evolution of HCl ceased, the flask was cooled and the melt was boiled with EtOH and filtered. The solid was dissolved in $CHCl_3$ and filtered through short pad of aluminum oxide to remove tars. The solution was concentrated under reduced pressure and the resulting solid was dissolved in toluene and subjected chromatography on column packed with silica gel (Merck 60, 70–230 mesh). Yellow crystals, 400 mg, 83%, mp. 232°C (toluene). Lit.[7] 232–234°C.

^{1}H NMR ($CDCl_3$): 8.64 (s, 1H), 8.62–8.60 (m, 2H), 8.12–8.10 (m, 2H), 8.06 (d, $J=9.3$ Hz, 1H), 7.65–7.64 (dd, $J=9.3$ Hz, 2.5 Hz, 1H), 7.59–7.53 (m, 4H), 7.52 (d, $J=2.5$ Hz, 1H), 7.46 (t, $J=7.4$ Hz, 1H), 7.33–7.30 (m, 5H), 7.20–7.17 (m, 4H), 7.10 (t, $J=7.4$ Hz, 2H).

^{13}C NMR ($CDCl_3$): 150.47, 147.57, 145.39, 144.25, 144.17, 140.07, 132.72, 129.70, 129.62, 129.50, 129.05, 129.02, 128.89, 127.42, 125.77, 125.27, 124.70, 123.47, 120.54, 119.34, 116.67.

N-(1-Naphtyl)-N,1,2,3-triphenyl-1H-pyrazolo[3,4-b]quinoline (FN-DPPQ)

Yellow crystals, mp. 167–168°C (toluene).

^{1}H NMR ($CDCl_3$): 8.08–8.06 (m, 2H), 8.05 (d, $J=9.3$ Hz, 1H), 8.00–7.99 (m, 1H), 7.93–7.92 (d, $J=8.5$ Hz, 1H), 7.84–7.83 (d, $J=8.3$ Hz, 1H), 7.71–7.69 (dd, $J=9.3$ Hz, 2.6 Hz, 1H), 7.57 (t, $J=8.0$ Hz, 2H), 7.54–7.50 (m, 3H), 7.48–7.42 (m, 2H), 7.41–7.40 (m, 1H), 7.37–7.34 (m, 1H), 7.32–7.25 (m, 4H), 7.19–7.14 (m, 3H), 7.04 (t, $J=7.4$ Hz, 1H).

^{13}C NMR ($CDCl_3$): 150.32, 148.12, 145.06, 144.85, 144.09, 143.39, 140.09, 135.41, 132.71, 130.99, 129.58, 129.37, 129.03, 128.97, 128.90, 128.82, 128.52, 128.36, 128.24, 127.39, 127.23, 126.80, 126.64, 126.42, 126.34, 125.78, 125.32, 125.21, 124.12, 122.64, 120.51, 116.89, 116.65.

Analysis calculated for $C_{38}H_{26}N_4$ 84.74C–4.87H–10.40N. Found 84.56C–4.66H–10.37N.

6-Carbazol-9-yl-1H-pyrazolo[3,4-b]quinoline (CBZ-DPPQ)

Yellow crystals, mp. 233–234°C

^{1}H NMR ($CDCl_3$): 8.97 (s, 1H), 8.67–8.65 (m, 2H), 8.41 (d, $J=9.0$ Hz, 1H), 8.22 (d, $J=2.3$ Hz, 1H), 8.18 (t, $J=7.5$ Hz, 4H), 8.01–7.98 (dd, $J=9.0$ Hz, 2.3 Hz, 1H), 7.64–7.59 (m, 4H), 7.53–7.50 (m, 3H), 7.46–7.43 (m, 2H), 7.38–7.32 (m, 3H).

^{13}C NMR ($CDCl_3$): 151.17, 147.08, 144.59, 140.96, 139.88, 133.82, 132.42, 130.89, 130.76, 130.37, 129.22, 129.17, 129.15, 127.56, 126.16, 126.12, 125.64, 125.09, 123.62, 120.77, 120.49, 120.34, 117.07, 109.71.

Analysis calculated for $C_{34}H_{22}N_4$: 83.93C–4.56H–11.51N. Found 83.89C–4.41H–11.34N.

Device fabrication and characterization: electroluminescent properties

We fabricated double layer OLEDs with the following structure: ITO/PEDOT:PSS/PVK+luminophore/ETM/Ca/Al, where luminophore are 1*H*-pyrazoloquinoline derivatives subsequently FF-DPPQ, FNA-DPPQ and CBZ-DPPQ (Figs. 1 and 2).

The anode substrates were prepared from commercially available glass slides with transparent ITO film (resistance
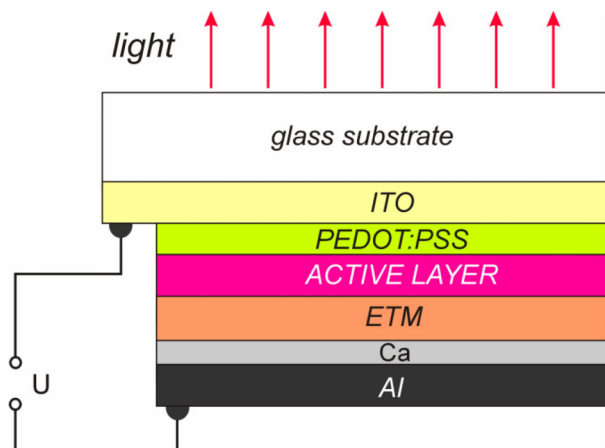
Figure 2 **Scheme for double layer organic electroluminescence diode (OLED) used for experiment**

Figure 4 **Current–voltage characteristics for electroluminescence devices ITO/PEDOT:PSS/PVK+luminophore/ETM/Ca/Al (luminophore=FF-DPPQ, FNA-DPPQ, CBZ-DPPQ) configurations: curves are labeled according to type of OLED active layer**

150 Ω sq^{-1}; Aldrich). Slides were ultrasonically cleaned in detergent solution and rinsed first in deionized water and next in tetrahydrofurane THF during 80 min. In the subsequent step, anode substrates were dried in technical vacuum at 100°C for 30 min. A solution of PEDOT:PSS [poly(ethylene-dioxythiophene)–polystyrenesulfonate] in water was spin coated onto a prea-cleaned slides dried in argon atmosphere and placed in vacuum for 30 min at 100°C for overnight. A mixture of appropriate luminophore (FF-DPPQ, FNA-DPPQ, CBZ-DPPQ) and a hole transporting material PVK was dissolved in tetrahydrofurane. The solution was deposited onto substrates by spin coating in argon to remove dissolved air at a spin speed of 1000 rev min^{-1} followed by drying at 70°C for 30 min to get rid of the traces of THF. Afterward an electron transporting material TRI-Q in 80% formic acid was spin cast on emission layer. After drying, 10 nm calcium and 100 nm aluminum layers were deposited onto the TRI-Q film.

The electroluminescence spectra of ITO/PEDOT:PSS/PVK+luminophore/ETM/Ca/Al were recorded using Shimadzu UV-Vis 2101 scanning spectrophotometer applying the direct current bias voltage in the forward direction (ITO, positive;
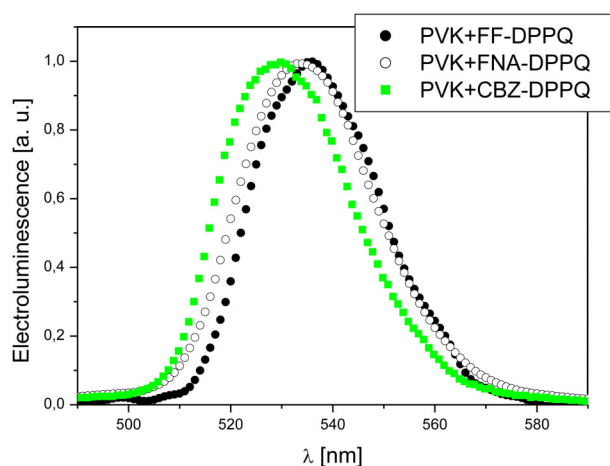
Ca/Al, negative). All measurements were performed at room temperature and all devices were displayed in air without encapsulation.

Results and discussion

Figure 3 shows the normalized steady state spectra of electroluminescence devices ITO/PEDOT:PSS/PVK+luminophore/ETM/Ca/Al configurations.

The devices doped with luminophores FF-DPPQ, FNA-DPPQ and CBZ-DPPQ emitted strong green light (Fig. 3 and Table 1). The spectral range of the electroluminescence for investigated materials is 527–535 nm. For PVK+FF-DPPQ, PVK+FNA-DPPQ and PVK+CBZ-DPPQ active layers, it corresponded to 535, 532 and 527 nm respectively. The spectral maxima for 527 nm containing OLED with the PVK+CBZ-DPPQ active layer are spectrally shifted to lower wavelength with respect to other luminophores (FF-DPPQ and FNA-DPPQ).

The current–voltage dependence demonstrate complimentary features with respect to the luminance–voltage characteristics of ITO/PEDOT:PSS/PVK+luminophore/Ca/Al OLED's devices (cf. Figs. 4 and 5).

The turn-on voltages extracted from lumen–voltage dependencies are listed in Table 1. The molecule FF-DPPQ corresponded to 10 V, the molecule FNA-DPPQ corresponded to 12 V and CBZ-DPPQ corresponded to 11 V.

The prepared compounds The maximally achieved brightness was about 800 cd m^{-2} for ITO/PEDOT:PSS/PVK+luminophore/ETM/Ca/Al electroluminescence devices with active layers PVK+FNA-DPPQ.

Figure 3 **Normalized steady state electroluminescence spectra of ITO/PEDOT:PSS/PVK+luminophore/ETM/Ca/Al (luminophore=FF-DPPQ, FNA-DPPQ, CBZ-DPPQ) OLEDs: curves are labeled according to type of OLED active layer**
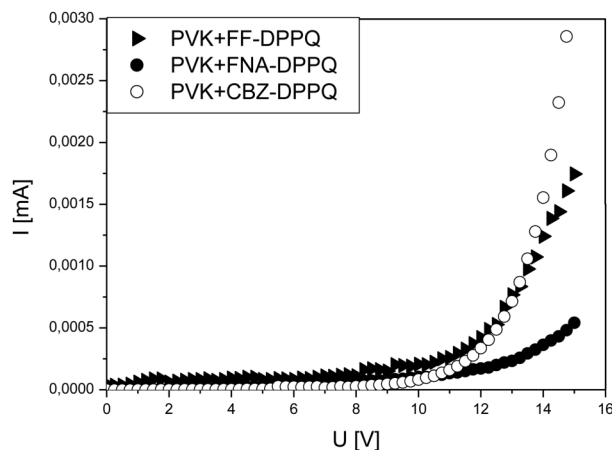
Table 1 **Principal parameters for investigated molecules**

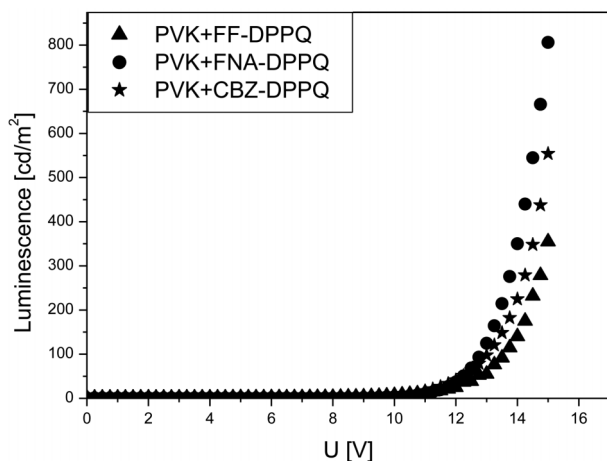| Molecule	$\lambda_{EL\ max}$/nm	Brightness/cd m^{-2}	V_{on}/V
FF-DPPQ	535	355	10
FNA-DPPQ	532	806	12
CBZ-DPPQ	527	554	11

Figure 5 Luminance–voltage characteristics for ITO/PEDOT:PSS/PVK+luminophore/ETM/Ca/Al (luminophore= FF-DPPQ, FNA-DPPQ, CBZ-DPPQ) OLEDs: curves are labeled according to type of OLED active layer

In this paper, we present the electroluminescence devices based on PVK active emitting layer doped with several 6-substituted 1,3-diphenylpyrazoloquinoline derivatives. We demonstrated measure electroluminescence spectra, luminance–voltage and current–voltage characteristics of the prepared double layer OLEDs. All the double layer devices exhibit strong green electroluminescence. In spite of the fact that pyrazoloquinolines exhibit some charge transporting properties (1×10^{-6}–3×10^{-5} cm^2 Vs^{-1}) comparable with PBD (1.9×10^{-5} cm^2 Vs^{-1}), we added an additional layer of electron transporting material based on quinoline TRI-Q.[39,40] The parameters of this device were comparable with the one we reported earlier.[32] It was multilayer device with the configuration ITO/NPB/CBP/TPBI:PQ/TPBI/MgAg where NPB and CBP were amorphous aromatic amine hole transporting materials and TPBI was used as electron transporting material. It means that present simplified device configuration can compete with the vacuum evaporated counterpart. The driving voltage in present experiment is relatively high,

but we hope that it can be reduced by modification of ETM (Table 1).

1*H*-Pyrazolo[3,4-*b*]quinolines **4a**–**c** for OLED fabrication were prepared in twofold way (Fig. 6). First, we applied palladium catalyzed aminoarylation of 6-bromo-1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline **3**. Bromoderivative **3a** is easily prepared in the reaction of **1** with *p*-bromoaniline according to the procedure developed by Brack.[41] The aminoarylation of various aromatic bromoderivatives is very convenient method of amine preparation, but in this case, a small amounts of some side products occurred. This impurities are very troublesome to remove so we applied and alternative procedure namely the reaction of 4-chloro-5-chloro-1,3-diphenyl-4-pyrazole-4-carbaldehyde **1** with p-*N*,*N*-diaryl substituted anilines **2a**–**c** resulting pyrazoloquinoline **4a**–**c**. In this case, the final product **4a**–**c** was easily purified with column chromatography. The amines **5a**–**c** were prepared in the reactions of *p*-fluoro(chloro)nitrobenzene with carbazole, diphenyl amine and *N*-phenyl-*N*-2-naphtyla-mine. Nitro compounds were reduced with hydrazine in the presence of palladium catalyst (10%Pd/charcoal). Electron transporting star burst quinoline TRI-Q was prepared according to literature procedure.[26]

Conclusions

To summarize, we have prepared a series of pyrazoloquinolines for solution processable organic light emitting devices. Green light emitting devices constructed using this compounds possess relatively high luminance. The only drawback is relatively high driving voltage. We expect to reduce it by modification of electron transporting materials.

Conflicts of interest

The authors declare that there are no conflicts of interest.
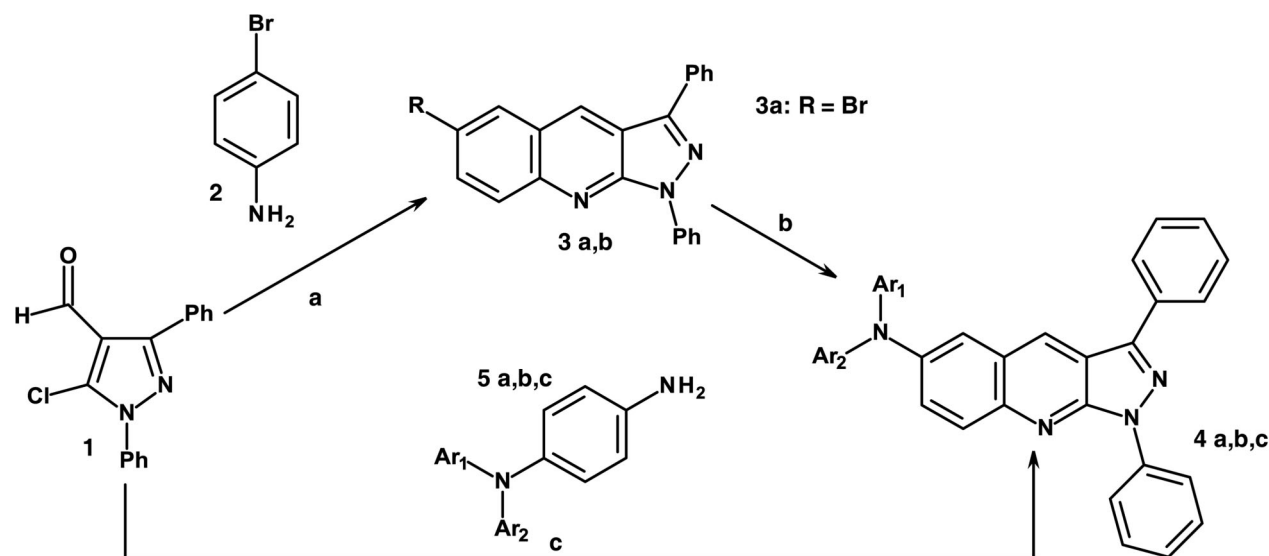
Acknowledgement

Figure 6 *a* melting 120–180°C, *b* 5a–c/Pd(0)/phosphine and *c* melting 140–200°C

References

1. U. Mitschke and P. Bäuerle: *J. Mater. Chem.*, 2000, **10**, 1471–1507.
2. L. S. Hung and C. H. Chen: *Mater. Sci. Eng. R*, 2002, **R39**, 143–222.
3. Y. Shirota and H. Kageyama: *Chem. Rev.*, 2007, **107**, 953–1010.
4. A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes: *Chem. Rev.*, 2009, **109**, 897–1091.
5. A. Mishra, C.-Q. Ma and P. Bäuerle: *Chem. Rev.*, 2009, **109**, 1141–1276.
6. J. E. Coughlin, Z. B. Henson, G. C. Welch and G. C. Bazan: *Acc. Chem. Res.*, 2014, **47**, (1), 257–270.
7. M. Pope, H. Kallman and P. Magnante: *J. Chem. Phys.*, 1963, **38**, 2042–2043.
8. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes: *Nature*, 1990, **347**, 539–541.
9. D. Braun and A. J. Heeger: *Appl. Phys. Lett.*, 1991, **58**, 1982–1984.
10. L. Duan, L. Hou, T.-W. Lee, J. Qiao, D. Zhang, G. Dong, L. Wang and Y. Qiu: *J. Mater. Chem.*, 2010, **20**, 6392–6407.
11. S. Setayesh, A. C. Grimsdale, T. Weil, V. Enkleman, K. Müllen, F. Meghdadi, E. J. W. List and G. Leising: *J. Am. Chem. Soc.*, 2001, **123**, 946–953.
12. D. Braun, G. Gustaffson, D. McBranch and A. J. Heeger: *J. Appl. Phys.*, 1992, **72**, 564–568.
13. C. J. Tonzola, M. M. Alam and S. A. Jenekhe: *Adv. Mater.*, 2002, **14**, 1086–1090.
14. X. Yang, D. Neher, D. Hertel and T. K. Däubler: *Adv. Mater.*, 2004, **16**, 161–166.
15. D. Neher, B. Łuczyńska, E. Dobruchowska, I. Głowacki, J. Ulański, F. Jasier, X. Yang and A. Danel: *J. Appl. Phys.*, 2006, **99**, 024505–024506.
16. T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, I. D. W. Samuel, S. C. Lo and P. L. Burn: *Appl. Phys. Lett.*, 2003, **82**, 4824–4826.
17. T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck: *Chem. Rev.*, 2007, **107**, (4), 1011–1065.
18. C. H. Chien, L. R. Kung, C. H. Wu, C. F. Shu, S. Y. Changand and Y. Chi: *J. Mater. Chem.*, 2008, **18**, 3461–3466.
19. K. Watanabe, D. Kumaki, T. Suzuki, E. Tokunaga and S. Tokito: *J. Photopolym. Sci. Technol.*, 2007, **20**, 39–42.
20. H.-W. Chang, Y.-T. Lee, M.-R. Tseng, M.-H. Jang, H.-C. Yeh, F.-T. Luo, H.-F. Meng, C.-T. Chen, Y. Chi, Y. Qiu, L. Duan, H.-W. Lin, S.-F. Horng and H.-W. Zan: *Synth. Met.*, 2014, **196**, 99–109.
21. F. Cacialli, B. S. Chuach, J. S. Kim, D. A. dos Santos, R. H. Friend, S. C. Moratti, A. B. Holmes and J. L. Bredas: *Synth. Met.*, 1999, **102**, 924–925.
22. M. M. Alam and S. A. Jenekhe: *Chem. Mater.*, 2002, **14**, 4775–4780.
23. M. S. Bayerl, T. Braig, O. Nuyken, D. C. Muller, M. Gross and K. Meerholz: *Macromol. Rapid Commun.*, 1999, **20**, 224–228.
24. Y. Zhang, R. Hreha, G. Jabbour, B. Kippelen, N. Peyghambrian and S. R. Marder: *J. Mater. Chem.*, 2002, **12**, 1703–1708.
25. S. Liu, X. Jiang, H. Ma, M. S. Liu and A. K.-Y. Yen: *Macromolecules*, 2000, **33**, 3514–3517.
26. E. Ahmed, T. Earmme and S. A. Jenekhe: *Adv. Funct. Mater.*, 2011, **21**, 3889–3899.
27. T. Earmme and S. A. Jenekhe: *Adv. Funct. Mater.*, 2012, **22**, 5126–5136.
28. T. Earmme and S. A. Jenekhe: *J. Mater. Chem.*, 2012, **22**, 4660–4668.
29. W. Jiang, H. Xu, X. Ban, G. Yuan, Y. Sun, B. Huang, L. Duan and Y. Qiu: *Org. Lett.*, 2014, **16**, 1140–1143.
30. K. Rechthaler, K. Rotkiewicz, A. Danel, P. Tomasik, K. Khatchatryan and G. Köhler: *J. Fluoresc.*, 1997, **7**, (4), 301–309.
31. J. Funaki, K. Imai, K. Araki, A. Danel and P. Tomasik: *Polish J. Chem.*, 2004, **78**, 843–850.
32. Y.-T. Tao, E. Balasubramaniam, B. Jarosz and P. Tomasik: *Chem. Mater.*, 2001, **13**, 1207–1212.
33. E. Gondek, A. Danel, J. Nizioł, P. Armatys, I. V. Kityk, P. Szlachcic, M. Karelus, T. Uchacz, J. Chwast and G. Lakshminarayana: *J. Lumin.*, 2010, **130**, (11), 2093–2099.
34. Y. Takahashi, T. Ito, S. Sakai and Y. Ishii: *J. Chem. Soc. D*, 1970, **17D**, 1065–1066.
35. Z. Weihui, X. Chen, Y. Shen: *J. Chem. Res.*, 2010, **34**, (7), 370–374.
36. S.-H. Lee, S. H. Kim and K. Jeonghun: *J. Nanosci. Nanotechnol.*, 2013, **13**, 4216–4222.
37. C.-S. Wu, J.-W. Wu and Y. Chen: *J. Mater. Chem.*, 2012, **22**, 23877–23884.
38. H.-Y. Wu, K.-L. Wang, D.-J. Liaw, K.-R. Lee and J.-Y. Lai: *J. Polym. Sci. Part A: Polym. Chem.*, 2010, **48A**, (7), 1469–1476.
39. A. R. Tamaeev, Z. He, G. H. W. Milburn, A. A. Kozlov, A. V. Vannikov, A. Danel and P. Tomasik: *Appl. Phys. Lett.*, 2000, **77**, 322–324.
40. A. P. Kulkarni, J. P. Tonzola, A. Babel and S. A. Jenekhe: *Chem. Mater.*, 2004, **16**, 4556–4573.
41. A. Brack: *Liebigs Ann. Chem.*, 1965, **681**, 105–110.
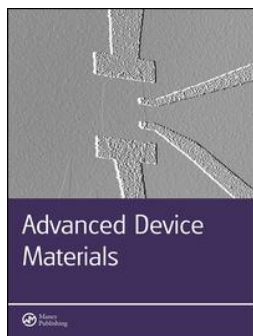
Solution processable double layer organic light emitting diodes (OLEDs) based on 6-*N*,*N*-arylsubstituted-1*H*-pyrazolo[3,4-*b*]quinolines

Andrzej Danel, Łukasz Chacaga, Tomasz Uchacz, Monika Pokladko-Kowar, Ewa Gondek, Paweł Karasiński & Bouchta Sahraoui