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# 3,6-Bis(indol-1-yl)-9-phenylcarbazoles as electroactive materials for electrophosphorescent diodes

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#### ABSTRACT

Four derivatives of 3,6-bis(indol-1-yl)-9-phenylcarbazole were synthesized by Ullmann-type coupling including those having methoxy groups at the different positions. Thermal, optical and photophysical properties of the synthesized materials were studied. All the synthesized 3,6-bis(indol-1-yl)-9-phenylcarbazoles are capable of glass formation with the glass transition temperatures ranging from 77 to 95 °C. They exhibit high thermal stability with the 5% weight loss temperatures ranging from 393 to 459 °C. Photoluminescence spectra of the dilute solutions of 3,6-bis(indol-1-yl)-9-phenylcarbazoles are characterized by two well-resolved vibrational peaks at ca. 390 nm and 405 nm. The solid films of the materials also exhibit well-resolved vibrational peaks, however the wavelengths of the maxima are red-shifted by ca. 10 nm. 3,6-Bis(indol-1-yl)-9-phenylcarbazoles were tested in the single-layer organic light emitting diodes as active materials and in phosphorescent light emitting diodes as host materials of emitting layers in combination with **Ir(Fppy)**<sub>3</sub> as a guest phosphor. Blue single-layer electroluminescent and electrophosphorescent devices with current efficiencies of 3,7–4,1 cd/A and 10.8–12.6 cd/A respectively were fabricated.

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# 1. Introduction

Starting from the first publication [1], organic light-emitting diodes (OLEDs) have attracted a great deal of interest because of their potential applications in full-color flat-panel displays and lighting sources [2–4]. In recent years, a lot of efforts have been concentrated on the development of electrophosphorescent light emitting devices (PHOLEDs) based on luminescent transitionmetal complexes because of high quantum efficiencies which can be attained in such devices [5–8]. Developing of highly efficient blue OLEDs attracts a special attention since their characteristics are so far inferior with respect to those of red or green ones [9]. High energies needed to produce blue light rise the special requirements for the photostability of the materials used in blue PHOLEDs [10]. The efforts to develop efficient and reliable blue PHOLEDs are aggravated by the lack of efficient chargetransporting materials with a wide energy gap for sufficient carrier injection [11]. In this work we report on the synthesis

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and characterization of glass-forming 3,6-bis(indol-1-yl)-9phenylcarbazoles (**BIPC**s) as well as on their thermal, optical, luminescent and photoelectrical properties. The performance of the synthesized materials in OLEDs was also studied. Two types of OLEDs were fabricated: single-layer blue light emitting devices based on **BIPC**s and blue-green phosphorescent devices obtained by simultaneous vacuum deposition from one crucible of host materials, **BIPC**s, and of the triplet emitter tris[2-(4,6difluorophenyl)pyridinato- $C^2$ ,N]iridium(III) complex (**Ir(Fppy)**<sub>3</sub>).

# 2. Experimental

# 2.1. Instrumentation

NMR spectra of deuterated chloroform (CDCl<sub>3</sub>) solutions were recorded using a Varian Unity Inova (300 MHz) apparatus. IR spectra of KBr pellets were obtained on a Perkin–Elmer Spectrum GX II FT-IR System spectrometer. Mass spectra (MS) were obtained using a Bruker Maxis 4G system. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. Melting points were measured with Electrothermal MEL-TEMP apparatus. Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q100 calorimeter with a heating/cooling rate







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of 10 °C/min under nitrogen. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 4000 apparatus with a heating rate of 20 °C/min under nitrogen. Ionization potentials (*I*<sub>n</sub>) of solid films were established by electron photoemission in air method as described earlier [12]. The samples for the  $I_p$  measurements were prepared by casting tetrahydrofuran solutions of the materials on aluminum plates pre-coated with methylmethacrylate and methacrylic acid copolymer adhesive layer. UV absorption and photoluminescence (PL) spectra of dilute tetrahydrofuran solutions (0.05 mM) were recorded at ambient conditions on a Perkin-Elmer Lambda 35 spectrometer and Perkin-Elmer LS55 fluorescence spectrometer respectively. UV absorption spectra of vacuum deposited films were recorded with Cary 5000 UV-VIS-NIR and Specord UV–Vis spectrometers. The electroluminescent devices ITO/CuI (12 nm)/BIPCs (30 nm)/Ca (40 nm)/Al (200 nm) and ITO/ Cul/BIPCs:Ir(Fppy)<sub>3</sub> (50 nm)/TCz1 (10 nm)/Ca (40 nm)/Al (200 nm) were fabricated by means of vacuum co-deposition of BIPCs and Ir(Fppy)<sub>3</sub> as reported earlier [13]. Copper iodide (CuI) was used as the hole injection layer [14]. 3,6-Di(9-carbazolyl)-9-(2-ethylhexyl) carbazole (TCz1) served as the electron-transporting layer [15]. The thickness of the obtained layers was measured by NanoCalc 2000 Reflectometry System. The active area of the obtained devices was  $3 \times 2$  mm<sup>2</sup>. To experimentally observe the triplet state emission, the luminescence at 77 K from vacuum deposited BIPCs films was measured at the delay time of 100 µs after an excitation pulse and using a detector with a large gate width of 200 ms. The current density-voltage-luminance (I-V-L) characteristics and electroluminescence (EL) spectra were recorded using a Programmable Test Power LED300E spectrometer HAAS-2000 with an integrated sphere (d = 0.3 m). All characteristics of the fabricated devices were recorded in ambient air without passivation.

# 2.2. Materials

9*H*-carbazole, 4-iodoanisole, 1*H*-indole, 5-methoxy-1*H*-indole, 9-phenylcarbazole, 18-crown-6, *o*-dichlorobenzene and copper powder were purchased either form Aldrich or Fluka. Potassium carbonate, potassium iodide, potassium iodate and glacial acetic acid were purchased either from Penta or Lach-Ner, Czech Republic. The materials were used as received. Solvents for column chromatography and crystallization of target compounds were additionally distilled.

9-(4-Anisyl)carbazole (**3b**) was prepared by modified Ullmann condensation of 9*H*-carbazole (**1**) with 4-iodoanisole (**2**) in similar way as described earlier [16]. 3,6-Diiodo-derivatives of 9-arylcarbazoles (**4a**–**b**) were obtained by the iodination of 9-phenylcarbazole (**3a**) or **3b** respectively according to Tucker [17].

# 2.2.1. The general procedure for the synthesis of 3,6-bis(indol-1-yl)-9-phenylcarbazoles

5 mmol of **4a** (2.48 g) or **4b** (2.63 g), 15 mmol of 1*H*-indole (**5a**, 1.76 g) or 5-methoxy-1*H*-indole (**5b**, 2.21 g) and 0.25 g 18-crown-6 were dissolved in 20 ml of *o*-dichlorobenzene. The mixture was heated up to 150 °C under nitrogen and 2.1 g of potassium carbonate and 0.95 g of copper powder were added. The reaction mixture was kept under reflux and controlled by TLC. After 4–6 h the complete consumption of diiodo-derivatives **4a–b** was observed and the heating was ended. The reaction mixture was cooled down to ambient temperature and filtered washing with *o*-dichlorobenzene which was further removed by vacuum distillation. The dark crude product was thereafter purified by column chromatography on silica-gel using the mixture of acetone and hexane (volume ratio 1–5) as an eluent and then recrystallized from the organic solvent indicated at the description of each compound.

#### 2.2.2. 3,6-Bis(indol-1-yl)-9-phenylcarbazole (BIPC)

Precipitated in methanol; recrystallized from hexane. Small white crystals. Yield 1.55 g (65%). M.p. 179–180 °C. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz) ppm: 6.71 (dd, 2H, aromatics,  $J^1 = 3.3$  Hz,  $J^2 = 0.7$  Hz), 7.13–7.26 (m, 4H, aromatics), 7.42 (d, 2H, aromatics, J = 3.3 Hz), 7.50–7.74 (m, 13H, aromatics), 8.21 (dd, 2H, aromatics,  $J^1 = 1.8$  Hz,  $J^2 = 0.7$  Hz). <sup>13</sup>CNMR (CDCl<sub>3</sub>, 75 MHz) ppm: 103.0, 110.3, 110.8, 116.9, 120.1, 121.0, 122.2, 123.5, 124.0, 127.0, 128.1, 128.7, 128.9, 130.1, 132.8, 136.6, 140.1. FT-IR (KBr) cm<sup>-1</sup>: 3101, 3047 (ν C–H aromatic), 1594, 1580, 1513, 1492, 1475 (ν C=C aromatic), 1332, 1312, 1278 (ν C–N aromatic), 884, 846, 814, 761, 741 (γ C–H aromatic). FW = 473.57. MS (APCI+) *m/z*: 474.2017 (M + H). Elemental analysis for C<sub>34</sub>H<sub>23</sub>N<sub>3</sub>: calc. C 86.23%, H 4.90%, N 8.87%; found C 86.34%, H 4.95%, N 8.96%.

# 2.2.3. 3,6-Bis(indol-1-yl)-9-(4-methoxyphenyl)carbazole acetone solvate [**BIPC1** · (CH<sub>3</sub>)<sub>2</sub>CO]

Recrystallized from acetone. Colorless rhomboid plates. Yield 1.99 g (79%). M.p. 126–127 °C. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz) ppm: 2.17 (s, 6H, CH<sub>3</sub>, acetone) 3.94 (s, 3H, OCH<sub>3</sub>), 6.71 (dd, 2H, aromatics,  $J^1 = 3.3$  Hz,  $J^2 = 1.1$  Hz), 7.13–7.26 (m, 6H, aromatics), 7.40–7.60 (m, 10H, aromatics), 7.69–7.74 (m, 2H, aromatics), 8.20 (d, 2H, aromatics, J = 1.6 Hz). <sup>13</sup>CNMR (CDCl<sub>3</sub>, 75 MHz) ppm: 55.6, 102.9, 110.3, 110.7, 115.3, 116.9, 120.1, 121.0, 122.2, 123.3, 123.9, 128.5, 128.8, 128.9, 129.6, 132.6, 140.6. FT-IR (KBr) cm<sup>-1</sup>: 3056, 3042 (v C–H aromatic), 2962, 2933, 2838 (v C–H aliphatic), 1709 (v C=O), 1609, 1582, 1513, 1491, 1457 (v C=C aromatic), 1333, 1314, 1292, 1280 (v C–N aromatic), 1247, 1216, 1028 (v C–O–C), 884, 833, 762, 747 (γ C–H aromatic), FW (**BIPC1**) = 503.59. MS (APCI+) *m/z*: 504.2119 (M + H). Elemental analysis for C<sub>35</sub>H<sub>25</sub>N<sub>3</sub>O·(CH<sub>3</sub>)<sub>2</sub>CO: calc. C 81.26%, H 5.56%, N 7.48%, O 5.70%; found C 81.05% H 5.62% N 7.54%.



Scheme 1. The synthetic route to 3,6-bis(indol-1-yl)-9-phenylcarbazoles.



Fig. 1. DSC thermograms of BIPC2.



Recrystallized from acetone. Small white crystals. Yield 2.02 g (76%). M.p. 200–201 °C. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz) ppm: 3.88 (s, 6H, OCH3), 6.62 (dd, 2H, aromatics,  $J^1 = 3.3$  Hz,  $J^2 = 0.7$  Hz), 6.88 (dd, 2H, aromatics,  $J^1 = 8.8$  Hz,  $J^2 = 2.2$  Hz), 7.16 (d, 2H, aromatics, *I* = 2.2 Hz), 7.93 (d, 2H, aromatics, *J* = 3.3 Hz), 7.44 (d, 2H, aromatics, *I* = 8.8 Hz), 7.49–7.59 (m, 5H, aromatics), 7.60–7.71 (m, 4H, aromatics), 8.19 (dd, 2H, aromatics,  $J^1 = 1.8$  Hz,  $J^2 = 0.7$  Hz). <sup>13</sup>CNMR (CDCl<sub>3</sub>, 75 MHz) ppm: 55.8, 102.6, 110.8, 111.1, 112.4, 116.6, 123.7, 127.0, 128.0, 129.1, 129.4, 130.1, 131.9, 132.9, 140.0, 154.4. FT-IR (KBr) cm<sup>-1</sup>: 3099, 3046, 3012 (v C–H aromatic), 2986, 2957, 2940, 2906, 2831 (v C-H aliphatic), 1622, 1598, 1579, 1491, 1465 (v C=C aromatic), 1353, 1334, 1289 (v C-N aromatic), 1258, 1229, 1212, 1070, 1034 (v C-O-C), 873, 863, 850, 825, 789, 763 (v C-H aromatic). FW = 533.62. MS (APCI+) m/z: 534.2221 (M + H). Elemental analysis for C<sub>36</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>: calc. C 81.03%, H 5.10%, N 7.87%, O 6.00%; found C 80.94%, H 5.22%, N 7.96%.

# 2.2.5. 3,6-Bis(5-methoxyindol-1-yl)-9-(4-methoxyphenyl) carbazole (**BIPC3**)

Recrystallized from tetrahydrofuran. Small white crystals. Yield 2.09 g (74%). M.p. 205–206 °C. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz) ppm: 3.87 (s, 6H, OCH<sub>3</sub>), 3.93 (s, 3H, OCH<sub>3</sub>), 6.62 (d, 2H, aromatics, J = 2.9 Hz), 6.87 (dd, 2H, aromatics,  $J^1 = 8.8$  Hz,  $J^2 = 2.6$  Hz), 7.12–7.19 (m, 4H, aromatics), 7.38 (d, 2H, aromatics, J = 3.3 Hz), 7.40–7.58 (m, 8H, aromatics), 8.18 (d, 2H, aromatics, J = 2.2 Hz). <sup>13</sup>CNMR (CDCl<sub>3</sub>, 75 MHz) ppm: 55.6, 55.9, 102.6, 110.7, 111.1, 112.4, 115.3, 116.6, 123.3, 123.7, 128.5, 129.2, 129.4, 129.6, 132.0, 132.8, 140.5, 154.4, 159.3. FT-IR (KBr) cm<sup>-1</sup>: 3082, 2995 (ν C–H aromatic), 2929, 2831 (ν C–H aliphatic), 1618, 1580, 1514, 1477 (ν C=C aromatic), 1340, 1298 (ν C–N aromatic), 1253, 1043, 1024 (ν C–O–C), 866, 829, 817, 795, 758 (γ C–H aromatic). FW = 563.64. MS (APCI+) *m/z*: 564.2327 (M + H). Elemental analysis for C<sub>37</sub>H<sub>29</sub>N<sub>3</sub>O<sub>3</sub>: calc. C 78.84%, H 5.19%, N 7.46%, O 8.52%; found C 79.44%, H 5.31%, N 7.59%.

#### Table 1

Thermal characteristics of BIPCs.

Material	m.p. <sup>a</sup> (°C)	$T_{g}^{a}(^{\circ}C)$	$T_{D1\%}^{b}$ (°C)	$T_{D5\%}^{b}(^{\circ}C)$
BIPC BIPC1 BIPC2 BIPC3	175 133 <sup>c</sup> 197 202	89 77 95	300 384 402 405	393 441 451 459

<sup>a</sup> Established by DSC.

<sup>b</sup> Established by TGA.

<sup>c</sup> Decomposition of acetone solvate.



**Fig. 2.** Normalized absorption and PL spectra (a) of solutions (square) and vacuum deposited (circle) **BIPCs** films, and low temperature fluorescence and phosphorescence spectra (b) of vacuum deposited **BIPCs** films.

# 3. Results and discussion

# 3.1. Synthesis and characterization

Heterogenous Ullmann-type coupling reaction using powdered copper as a catalyst [18] was found to be a convenient method for the synthesis of *N*-indolyl-substituted carbazoles from *N*-aryl-3,6-diiodocarbazoles. The target compounds were obtained in good

Table 2		
Optical and photophysical	characteristics of BII	PCs and Ir(Fppy) <sub>3</sub> .

Material	BIPC	BIPC1	BIPC2	BIPC3	Ir(Fppy) <sub>3</sub>
$\lambda_{\rm sol.}^{\rm abs}$ (nm)	251, 270,	251, 271,	253, 278,	251, 278,	-
	296, 349	292*, 352	306, 352	308, 353	
λ <sup>abs</sup> (nm)	312, 375	312, 376	315, 377	312, 367	276, 357,
					390
λ <sup>abs</sup> (nm)	397	398	395	396	_
$\lambda_{sol.}^{PL}$ (nm)	387, 404	391, 406	394, 408	396, 409	_
$\lambda_{\text{film}}^{\text{PL}}$ (nm)	396*, 411	397, 415	398, 416	404, 418	-
$\lambda_{\text{film}}^{\text{PL}}(77 \text{ K}) (\text{nm})$	393, 415	396, 421	397, 421	403, 426	-
$\lambda_{\text{film}}^{\text{phos}}$ (nm)	442	454, 492	454, 494	453	471, 500
$I_{\rm p} ({\rm eV})$	5.68	5.66	5.52	5.45	-
$E_{\rm g}~({\rm eV})$	3.12	3.12	3.14	3.13	-
$E_{LUMO}$ (eV)	-2.56	-2.54	-2.38	-2.32	-

 $^{abs}$  – absorption,  $^{PL}$  – photoluminescence,  $^{phos}$  – phosphorescence,  $_{sol.}$  – dilute solutions,  $_{film}$  – films,  $_{on}$  – onset of absorption of films,  $I_p$  – ionization potential of solid state (attributed to  $E_{HOMO}$ ),  $E_g$  – optical band-gap (evaluated according to  $\lambda_{on}^{abs}$ ), \* – shoulder. LUMO levels were calculated on assuming that  $E_g = E_{HOMO} - E_{LUMO}$ .



Fig. 3. Electron photoemission spectra of BIPCs films.

yields of 65–79% after all the purification procedures. A three-step synthetic route which is presented in Scheme 1 included *N*-arylation of 9*H*-carbazole (1) followed by the iodination of *N*-arylcarbazoles **3a**–**b**. Diiodo-derivatives **4a**–**b** were obtained in good yields and they were further used for C–N coupling reaction with indoles **5a**–**b** to synthesize four new 3,6-bis(indol-1-yl)-9-phenylcarbazoles, referred as **BIPC**, **BIPC1**, **BIPC2** and **BIPC3** (the number was added to the abbreviation according to the amount of methoxy substituents in the molecule).

The obtained materials were found to be well-soluble in common organic solvents such as tetrahydrofuran and chloroform.

# 3.2. Thermal properties

The ability of glass formation of **BIPC**s was explored by DSC. All the synthesized 3,6-bis(indol-1-yl)-9-phenylcarbazoles were isolated after the synthesis and purification as crystalline materials and exhibited well-defined melting signals in the first DSC heating scans. When the melted samples were cooled down during DSC experiments, only the glass transitions were observed with no signals of crystallization of the substances. When the obtained glassy samples were heated again, only glass-to-liquid transitions were observed. For the illustration of the above stated, DSC curves of **BIPC2** are shown in Fig. 1. The values of glass transition temperatures ( $T_g$ ) are given in Table 1.

The established T<sub>g</sub> values for **BIPC**s are situated around 90 °C except that of **BIPC1**, the  $T_{g}$  of which was found to be lower by more than 10 °C in comparison to those of the rest of the materials. The presence of methoxy substituents at the C-5 positions of indole moieties slightly increases glass-transition temperatures of the derivatives. The introduction of methoxy group apparently elongates indole moiety in the direction across its spinning axis (C-N bond) and the rotation of this moiety becomes slightly hindered in bulk material which results in the higher  $T_g$  of **BIPC2** (95 °C) among these derivatives. In the case when methoxy substituent is present in the C-4 position of phenyl ring, i.e. along its spinning axis (C-N bond), it apparently makes this structure more flexible and decreases the  $T_g$  of **BIPC1** down to 77 °C. As the both of these effects take place in the molecule of **BIPC3**, the  $T_{g}$  of this material is close to the  $T_g$  of non-substituted **BIPC** (92 and 89 °C respectively).

Thermal stability of 3,6-bis(indol-1-yl)-9-phenylcarbazoles was examined by TGA. Their 5% weight loss temperatures ( $T_{D5\%}$ ) range



Fig. 4. Electroluminescence spectra of single-layer devices (a); current density-voltage and luminance-voltage characteristics (b) and current efficiency-current density characteristics and electroluminescent quantum yields (c) of single layered devices.

from 393 to 459 °C (Table 1). The thermal stability of **BIPC** having no methoxy groups is inferior with respect of that of methoxysubstituted derivatives. The introduction of methoxy substituents increases 5% weight loss temperatures by ca. 50-60 °C. To our knowledge, there are few reports considering low-molar-mass methoxy-substituted tertiary aromatic amines and nonsubstituted their analogs [19–22]. Yet, the thermal stability of the materials was discussed in neither of the referred papers. We suppose that the initial loss of weight is more determined by evaporation of a substance than by chemical decomposition. A sudden loss of weight occurs only above 350 °C or even 400 °C, when the samples are well above their melting points (Table 1). A faster loss of weight in the initial phase (up to 300-350 °C) is characteristic of non-substituted derivative (BIPC), while the methoxy-substituted counterparts of BIPC lose only less than 1% of their weight up to 350 °C (compare  $T_{D1\%}$  and  $T_{D5\%}$  values in Table 1). An introduction of methoxy substituents apparently enhances intermolecular interactions due to enhanced polarity of the molecules, which results into lower evaporation rate of the melts as well as of decomposition products.

#### 3.3. Optical and photophysical properties

Absorption and photoluminescence (PL) spectra of the solu tions and vacuum deposited films of 3,6-bis(indol-1-yl)-9phenylcarbazoles are shown in Fig. 2. The wavelengths of absorption and PL maxima are summarized in Table 2. Absorption spectra of the dilute solutions of 3,6-bis(indol-1-yl)-9-phenylcarbazoles are similar. They are characterized by four peaks at around 250, 275, 300 and 350 nm. The lowest-energy absorption bands and the absorption edges of the films exhibit small red-shifts with respect of those of the dilute solutions which can be attributed to the enhanced intermolecular interactions in condensed material. The influence of methoxy substituents on the position and intensity of the lowest-energy absorption band (ca. 350 nm) as well as to the wavelength of absorption edge is negligible. The onset absorption (which is determined by  $S_0 \rightarrow S_1$  transitions) of all the derivatives is observed at around 385 nm for dilute solutions and near 400 nm for the films. The latter value corresponds to the optical band-gap  $E_g$  of ca. 3.1 eV. PL spectra of the dilute solutions of 3,6-bis(indol-1-yl)-9-phenylcarbazoles are characterized by two well-resolved vibrational peaks at ca. 390 nm and 405 nm. Since molecular fragments of carbazole and indole exhibit emission below 360 nm [23,24] the observed fluorescence band at 390 nm can be attributed to the excitation of the whole molecules. The solid films of 3,6-bis(indol-1-yl)-9-phenylcarbazoles also exhibit well-resolved vibrational peaks, however the wavelength of maxima are at ca. 400 nm and 415 nm. These red-shifts of up to 10 nm in the fluorescence of films in respect to those of the solutions are apparently caused both by the negligible reabsorption of fluorescence and by the slight reciprocal influence of neighboring molecules in the films [25]. The above presented analysis of UV and fluorescence spectra of 3,6-bis(indol-1-yl)-9-phenylcarbazoles show that absorption and fluorescence centers of these compounds are mainly the same both in the solutions and in the films.

The phosphorescence spectra of the films of 3,6-bis(indol-1-yl)-9-phenylcarbazoles recorded at 77 K exhibit emission peaks that



Fig. 5. Electroluminescence spectra of electrophosphorescent devices ITO/Cul/BIPCs: Ir(Fppy)<sub>3</sub>/TCz1/Ca/Al (a), chemical structure of Ir(Fppy)<sub>3</sub> (b), CIE chromaticity diagram and photo of the electrophosphorescent device based on BIPC3: Ir(Fppy)<sub>3</sub> (c).

can be attributed to a sandwich excimer of adjacent carbazole moieties [26]. High triplet-levels (ca. 2.7 eV) of **BIPC**s give a possibility of using these materials as hosts for blue PHOLEDS [27].

lonization potentials  $(I_p)$  of the solid films of **BIPC** and its methoxy-substituted derivatives were estimated from electron photoemission spectra, which are presented in Fig. 3. The values of  $I_p$  are given in Table 2. The effect of methoxy-substitution at the phenyl ring on the energy levels of **BIPC** derivatives seems to be negligible as the  $I_p$  values of **BIPC** and **BIPC1** are, in essence, the same. The values of  $I_p$  of **BIPC2** and **BIPC3** are also close, however somewhat lower (by ca. 0.2 eV) than those of **BIPC** and **BIPC1** apparently because of methoxy-substitution at indole moieties.

#### 3.4. Electroluminescent single-layer devices

The electroluminescence (EL) spectra of the single-layer devices (Fig. 4a) based on BIPC1 and BIPC2 are identical to the PL spectra of the films, while EL spectra of the devices based on BIPC and BIPC3 are broadened as compared to the PL spectra of the films of the corresponding compounds. EL spectra of the devices based on BIPC and **BIPC3** are characterized by tree well-defined narrow peaks. Two high energy peaks correspond to those of fluorescence spectra of the films of BIPC and BIPC3 (Fig. 2b, Table 2) while the third one is due to excimer emission. Excimers are formed due to resonance interactions of a molecular exciton with the neighboring nonexcited molecules [28]. Fig. 4b and c shows characteristics of the single-laver electroluminescent structures ITO/CuI/BIPCs/Ca/Al. The current density-voltage curves of the devices show turn-on voltage Von of 4.0-6.2 V and the devices exhibit current efficiency values of 3.7-4.1 cd/A, which are comparable to those of the similar devices [29].

# 3.5. 3,6-Bis(indol-1-yl)-9-phenylcarbazoles as hosts for phosphorescent light-emitting diodes

In organic phosphorescent light emitting devices (PHOLEDs), host materials of the emitting layers are of great importance [11]. The host materials used for the transition metal-ligand complexes have to show good charge-transporting properties and high triplet energy that allows efficient exciton confinement on the guest molecules [10]. Because of favorable optical and electroluminescent properties of BIPCs we have used these materials as hosts for PHOLEDs with the commercial Ir(Fppy)<sub>3</sub> (Fig. 5b) guest phosphor. The triplet energy of 3,6-bis(indol-1-yl)-9-phenylcarbazoles is more than by 0.1 eV larger than that of Ir(Fppy)<sub>3</sub> [30]. The fluorescence of **BIPC**s partially overlap with the absorption band of Ir(Fppy)<sub>3</sub> (Fig. 2, Table 1). Thus the efficient Förster energy transfer is expected to take place from BIPCs to Ir(Fppy)<sub>3</sub> [31]. Electroluminescence maxima of the devices based on BIPCs:Ir(Fppy)3 (Fig. 5a) are observed at 476 nm and 500 nm The shape of the spectra of electroluminescence is similar to that of PL spectra of the solid films of Ir(Fppy)<sub>3</sub> [30,32]. This observation confirms that electrophosphorescence is naturally the emission of the devices. The current density-voltage curves of the devices show turn-on voltage  $V_{on}$  of 6.8–8.0 V and the devices exhibit current efficiency values of 10.8-12.6 cd/A (Fig. 6). CIE chromaticity coordinates (x, y) of the devices ITO/CuI/BIPCs:Ir(Fppy)<sub>3</sub>/TCz1/Ca/Al exhibiting blue-to-green color were found to be (0.23, 0.44) (Fig. 5c). Though the emitting color of the device was not deepblue, it is expected to be useful in other applications such as blue-green displays and lighting [33]. Lower turn-on voltage of devices based on BIPC2 and BIPC3 can be explained by lower ionization potentials  $(I_p)$  of the solid films and respectively lower potential barrier for holes. However the lower current efficiency was observed for the devices based on **BIPC2** and **BIPC3** apparently



**Fig. 6.** Current density-voltage and luminance-voltage characteristics (a) and current efficiency – current density characteristics and electroluminescent quantum yields (b) for electrophosphorescent devices ITO/Cul/**BIPCs:Ir(Fppy)**<sub>3</sub>/**TCz1**/Ca/Al.

due to higher current density caused by non-radiative recombination [34].

# 4. Summary

In summary, we have synthesized 3,6-bis(indol-1-yl)-9phenylcarbazole and three its methoxy-substituted derivatives and studied the properties of the synthesized compounds. They exhibit high thermal stability with the 5% weight loss temperatures ranging from 393 to 459 °C. All the compounds prepared form glasses with the glass transition temperatures ranging from 77 to 95 °C. **3,6-Bis(indol-1-yl)-9-phenylcarbazoles** were tested in the single-layer organic light emitting diodes as active materials and in phosphorescent light emitting diodes as host materials of emitting layers in combination with **Ir(Fppy)**<sub>3</sub> as a guest phosphor. The maximum brightness of the fabricated single-layer electroluminescent devices was ca. 1000 cd/m<sup>2</sup> with current efficiency of 4.0 cd/A and that of electrophosphorescent devices was ca. 11,000 cd/m<sup>2</sup> with current efficiency of 12.2 cd/A.

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# References

- Tang CW, VanSlyke SA. Organic electroluminescent diodes. Appl Phys Lett 1987;51:913-5.
- [2] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, et al. Light-emitting-diodes based on conjugated polymers. Nature 1990;347:539–41.
- [3] Huang JH, Su JH, Li X, Lam MK, Fung KM, Fan HH, et al. Bipolar anthracene derivatives containing hole- and electron-transporting moieties for highly efficient blue electroluminescence devices. J Mater Chem 2011;21:2957–64.
- [4] Huang JH, Su JH, Tian H. The development of anthracene derivatives for organic light-emitting diodes. J Mater Chem 2012;22:10977–89.
- [5] Baldo MA, O'Brien DF, You Y, Shoustikov A, Sibley S, Thompson ME, et al. Highly efficient phosphorescent emission from organic electroluminescent devices. Lett Nature 1998;395:151–4.
- [6] Köhler A, Wilson JS, Friend RH. Fluorescence and phosphorescence in organic materials. Adv Mater 2002;14:701–7.
- [7] D'Andrade B. Lighting: white phosphorescent LEDs offer efficient answer. Nat Photon 2007;1:33–4. http://www.nature.com/nphoton/journal/v1/n1/full/ nphoton.2006.45.html - a1#a1.
- [8] Adachi C, Baldo MA, Thompson ME, Forrest SR. Nearly 100% internal phosphorescence efficiency in an organic light emitting device. J Appl Phys 2001;90:5048-51.
- [9] Liu C, Gu Y, Fu Q, Sun N, Zhong C, Ma D, et al. Non-doped deep-blue organic light-emitting diodes with color stability and very low efficiency roll-off: solution-processable small-molecule fluorophores by phosphine oxide linkage. Chem Eur J 2012;18:13828–35.
- [10] Seidler N, Reineke S, Walzer K, Lüssem B, Tomkeviciene A, Grazulevicius JV, et al. Influence of the hole blocking layer on blue phosphorescent organic light-emitting devices using 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole as host material. Appl Phys Lett 2010;96:093304.
- [11] Xiao L, Chen Z, Qu B, Luo J, Kong S, Gong Q, et al. Recent progresses on materials for electrophosphorescent organic light-emitting devices. Adv Mater 2011;23:926–52.
- [12] Malinauskas T, Daskeviciene M, Kazlauskas K, Su HC, Grazulevicius JV, Jursenas S, et al. Multifunctional red phosphorescent bis-cyclometallated iridium complexes based on 2-phenyl-1,2,3-benzotriazole ligand and carbazolyl moieties. Tetrahedron 2011;67:1852–61.
- [13] Tomkute-Luksiene D, Keruckas J, Malinauskas T, Simokaitiene J, Getautis V, Grazulevicius JV, et al. 2-Phenyl-1,2,3-benzotriazole Ir(III) complexes with additional donor fragment for single-layer PhOLED devices. Dyes Pigm 2013;96:278–86.
- [14] Stakhira P, Cherpak V, Volynyuk D, Ivastchyshyn F, Hotra Z, Tataryn V, et al. Characteristics of organic light emitting diodes with copper iodide as injection layer. Thin Solid Films 2010;518:7016–8.
- [15] Stakhira P, Khomyak S, Cherpak V, Volyniuk D, Simokaitiene J, Tomkeviciene A, et al. Blue organic light-emitting diodes based on pyrazoline phenyl derivative. Synth Met 2012;162:352–5.
- [16] Matoliukstyte A, Grazulevicius JV, Reina JA, Jankauskas V, Montrimas E. Synthesis and properties of glass-forming condensed aromatic amines with reactive functional groups. Mat Chem Phys 2006;98:324–9.
- [17] Tucker SH. Iodination in the carbazole series. J Chem Soc 1926;1:546-53.

- [18] Gauthier S, Frechet JMJ. Phase-transfer catalysis in the Ullmann synthesis of substituted triphenylamines. Synthesis 1987;4:383–5.
- [19] Ishikawa W, Inada H, Nakano H, Shirota Y. Starbust molecules for amorphous molecular materials: synthesis and morphology of 1,3,5-tris(diphenylamino) benzene and its methyl-substituted derivatives. Mol Cryst Liq Cryst 1992;211: 431–8.
- [20] Thelakkat M, Fink R, Haubner F, Schmidt HW. Synthesis and properties of novel hole transport materials for electroluminescent devices. Macromol Symp 1998;125:157–64.
- [21] Ishikawa W, Noguchi K, Kuwabaru Y, Shirota Y. Novel amorphous molecular materials: the starburst molecule 1,3,5-tris[N-(4-diphenylaminophenyl)phenylamino]benzene. Adv Mater 1993;5:559–61.
- [22] Thelakkat M, Schmidt HW. Synthesis and properties of novel derivatives of 1,3,5-tris(diarylamino)benzenes for electroluminescent devices. Adv Mater 1998;10:219–23.
- [23] Grazulevicius JV, Soutar I, Swanson L. Photophysics of carbazole-containing systems. 3. Fluorescence of carbazole-containing oligoethers in dilute solution. Macromolecules 1998;31:4820–7.
- [24] Kirkus M, Lygaitis R, Tsai MH, Grazulevicius JV, Wu CC. Triindolylmethanebased high triplet energy glass-forming electroactive molecular materials. Synth Met 2008;158:226–32.
- [25] Tomkeviciene A, Grazulevicius JV, Kazlauskas K, Gruodis A, Jursenas S, Ke TH, et al. Impact of linking topology on the properties of carbazole trimers and dimmers. J Phys Chem C 2011;115:4887–97.
- [26] Hoffmann ST, Schrogel P, Rothmann M, Albuquerque RQ, Strohriegl P, Kohler A. Triplet excimer emission in a series of 4,4'-bis(N-carbazolyl)-2,2'biphenyl derivatives. J Phys Chem B 2011;115:414–21.
- [27] Tsai MH, Hong YH, Chang CH, Su HC, Wu CC, Matoliukstyte A, et al. 3-(9-Carbazolyl)carbazoles and 3,6-di(9-carbazolyl)carbazoles as effective host materials for efficient blue organic electrophosphorescence. Adv Mater 2007;19:862–6.
- [28] Kalinowski J. Excimers and exciplexes in organic electroluminescence. Mater Sci (Poland) 2009;27:735–56.
- [29] Gebeyehu D, Walzer K, He G, Pfeiffer M, Leo K, Brandt J, et al. Highly efficient deep-blue organic light-emitting diodes with doped transport layers. Synth Met 2005;148:205–11.
- [30] Endo A, Adachi C. Photoluminescence characteristics of tris(2phenylquinoline)iridium(III) dispersed in an iridium complex host layer. Chem Phys Lett 2009;483:224–6.
- [31] Tse SC, Tsung KK, So SK. Single-layer organic light-emitting diodes using naphthyl diamine. Appl Phys Lett 2007;90:213502.
- [32] Endo A, Suzuki K, Yoshihara T, Tobita S, Yahiro M, Adachi C. Measurement of photoluminescence efficiency of Ir(III) phenylpyridine derivatives in solution and solid-state films. Chem Phys Lett 2008;460:155–7.
- [33] Shen H, Wang S, Wang H, Niu J, Qian L, Yang Y, et al. Highly efficient bluegreen quantum dot light-emitting diodes using stable low-cadmium quaternary-alloy ZnCdSSe/ZnS core/shell nanocrystals. ACS Appl Mater Interfaces 2013;5:4260–5.
- [34] Köhler A, Bässler H. Triplet states in organic semiconductors. Mater Sci Eng R 2009;66:71–109. http://www.sciencedirect.com/science/article/pii/ S0927796X09000886-aff2#aff2.