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3-(*N*,*N*-Diphenylamino)carbazole Donor Containing Bipolar Derivatives with Very High Glass Transition Temperatures as Potential TADF Emitters for OLEDs

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Abstract: Well-defined electroactive bipolar derivatives of new structure have been synthesized from 3-(*N*,*N*-diphenylamino)-9H-carbazole and bis(4-fluorophenyl)sulfone, 4-fluorophenylsulfone or 4,4′-difluorobenzophenone, respectively. The full characterization of their structure is described. The amorphous materials with very high glass transition temperatures of 111–173 °C also possess high thermal stability, with onset decomposition temperatures of 351–398 °C. Some of the compounds having the best solubility were tested as the emitters dispersed in 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) host for preparation of organic light emitting diodes (OLEDs). A device containing 15 wt% of the guest bis[4-{3-(*N*,*N*-diphenylamino)carbazol-9-yl}phenyl] sulfone demonstrated the best overall characteristics with maximum brightness exceeding 2630 cd/m^2, current efficiency of 3.2 cd/A, power efficiency of 2.2 lm/W, and external quantum efficiency exceeding 1.7% at 100 cd/m^2.

Keywords: amorphous material; synthesis; organic light emitting diode; efficiency; emitter

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1. Introduction

Blue light emitting derivatives, particularly the pure organic materials with suitable light colour and high morphological stability, are very relevant in the OLEDs industry [1–6]. Earlier widely investigated phosphorescence metallic complexes and phosphorescent OLEDs contain noble metals, were environment-hazardous, and more expensive [7–12]. They especially suffer from stability of the devices and from not-satisfied light colours [13–17]. Achieving a suitable light colour and suitable morphological stability in pure organic emitters has been a hot investigations field in last years. At this time, very actively studied thermally activated delayed fluorescent (TADF) emitters have also solved the disadvantage that only singlet excitons are used for traditional OLEDs [18–22].

Low molar mass organic derivatives that can form stable amorphous films are known as molecular glasses or amorphous molecular materials. The derivatives demonstrate transparency, good film forming, and homogeneous properties, and are widely investigated in terms of scientific research and technological development [23–28]. Aromatic amines as molecular glasses are in the group of charge-transporting and light emitting layer derivatives and are well known in OLEDs field applications [29–32]. The main advantages of the electroactive low molar mass compounds against polymers are their low viscosity after melting, opportunity of purification in chromatographic procedures, and large variety of synthesis methods [33,34].

In this paper, we present well-defined electroactive bipolar derivatives containing 3-(*N*,*N*-diphenylamino)-9H-carbazole as donor and (bis)phenylsulfone or benzophenone as acceptor fragments. Such structures are interesting as potential TADF emitting materials and we tested the derivatives in this field. 3-(*N*,*N*-Diphenylamino)carbazole fragment is useful for emitting properties of the materials, and the bipolar nature is responsible for suitable transfer of charges in the emitting layer. Variation of the rigid aromatic structures also enabled us to synthesize the group of amorphous materials as having very high values of T_g (glass transition temperature) and emitting derivatives for OLEDs.

2. Experimental

2.1. Materials

4-Fluorophenyl phenyl sulfone, *9H*-carbazole (**1**), 4,4′-difluorobenzophenone, 60% sodium hydride (NaH), bis(4-fluorophenyl) sulfone, *N*,*N*-dimethylformamide (DMF), dichloromethane, acetone, acetic acid (CH_3COOH), *p*-toluenesulfonyl chloride, methanol, diphenylamine, chloroform, tetrahydrofurane (THF), dimethyl sulfoxide (DMSO), 10% hydrochloric acid (HCl), 18-crown-6, copper (Cu), copper(I) iodide (CuI), K_2CO_3, KOH, KI, KIO_3, and Na_2SO_4 were acquired from Aldrich (Darmstadt, Germany).

3-Iodo-*9H*-carbazole (**2**) was obtained from the *9H*-carbazole (**1**) by using its Tucker iodination reaction with KI and KIO_3 according to the methodic described in the literature [35].

3-Iodo-9-tosylcarbazole (**3**) was prepared in reaction of the 3-iodo-*9H*-carbazole (**2**) with *p*-toluenesulfonyl chloride according to the procedure described in the literature [36].

3-(*N*,*N*-diphenylamino)-9-tosylcarbazole (**4**) CuI (0.94 g, 4.94 mmol), Cu (0.34 g, 5.350 mmol), and K_2CO_3 (1.54 g, 11.16 mmol) have been added to a solution of compound **3** (2.0 g, 4.47 mmol), diphenylamine (1.14 g, 6.74 mmol), and 18-crown-6 (1.18 g, 4.46 mmol) in dry DMF (30 mL) under N_2 atmosphere. The obtained mixture was stirred for 48 h at 155 °C, then cooled to room temperature, and poured into water and extracted using chloroform. The combined extract was dried over anhydrous Na_2SO_4. The crude compound has been purified by silica gel column chromatography using THF and hexane mixture (vol. ratio 1:30) as an eluent. Yield: 1.5 g of white product (69%). MS ($APCI^+$, 20 V): 511.13 ([M+Na], 100%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.21 (d, 1H, J = 8.4 Hz, Ar), 8.12 (d, 1H, J = 8.6 Hz, Ar), 7.65 (d, 3H, J = 8.4 Hz, Ar), 7.54 (s, 1H, Ar), 7.42–7.35 (m, 3H, Ar), 7.24–7.13 (m, 6H, Ar), 7.11–6.98 (m, 6H, Ar), 6.97–6.85 (m, 2H, Ar), 2.24 (s, 3H, CH_3).

3-(*N*,*N*-diphenylamino)-9H-carbazole (**5**). To a solution of compound **4** (0.7 g, 1.43 mmol) in DMSO (6 mL):THF (12 mL):water (2 mL) mixture, powered KOH (0.16 g, 2.85 mmol) was added. The resulting mixture was stirred at reflux for 1.5 h. After cooling to room temperature, 10% HCl (20 mL) was added, followed by the addition of water (10 mL) and methanol (5 mL). The precipitates were separated by filtration and then washed with water. The crude material was recrystallized from dichloromethane/methanol mixture. Yield: 0.4 g of white product (85%). MS ($APCI^+$, 20 V): 335.26 ([M+H], 100%). ^{1}H NMR (400 MHz, DMSO, δ): 11.32 (s, 1H, NH), 8.02 (d, 1H, J = 8.0 Hz, Ar), 7.92 (s, 1H, Ar), 7.50 (t, 2H, J = 8.0 Hz, Ar), 7.37 (t, 1H, J = 7,6 Hz), 7.24 (t, 4H, J = 7.8 Hz), 7.17 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.6 Hz, Ar), 7.10 (t, 1H, J = 7.4 Hz, Ar), 6.99 (d, 4H, J = 8.0 Hz, Ar), 6.93 (t, 2H, J = 7.2 Hz, Ar).

Bis[4-{3-(*N*,*N*-diphenylamino)carbazol-9-yl}phenyl] sulfone (**6**). 0.35 g (1.05 mmol) of compound **5** and 0.04 g (1.7 mmol) of 60% NaH have been stirred in 10 mL of DMF under nitrogen for 30 min at room temperature. Next, 0.11 g (0.31 mmol) of bis(4-fluorophenyl) sulfone was added into the mixture. The obtained solution was stirred at 100 °C for 2 h. After TLC tests, the reaction mixture was cooled and quenched by the addition of ice water. The organic materials were extracted with dichloromethane. The extract was dried using Na_2SO_4. The crude compound was crystallized from methanol. Yield: 0.35 g of yellow material (92%). MS ($APCI^+$, 20 V): 883.27 ([M+H], 100%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18 (d, 4H, J = 8.8 Hz, Ar), 7.89 (d, 2H, J = 7.6 Hz, Ar), 7.82 (s, 2H, Ar), 7.74 (d, 4H, J = 8.4 Hz, Ar), 7.43–7.34 (m, 2H, Ar), 7.35–7.28 (m, 4H, Ar), 7.23–7.09 (m, 12H, Ar), 7.07–6.96 (m, 8H, Ar), 6.95–6.83 (m, 4H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 148.42, 142.75, 141.70, 140.40, 139.30, 136.80, 129.76, 129.18, 127.02, 126.59, 125.64, 125.13, 123.78, 123.01, 121.98, 121.04, 120.82, 118.23, 110.57, 109.75.

4-{3-(*N*,*N*-diphenylamino)carbazol-9-yl}phenyl phenylsulfone (**7**). 0.4 g (1.20 mmol) of derivative **5** and 0.11g (4.6 mmol) of 60% NaH were stirred in 10 mL of DMF under nitrogen for 30 min at room temperature. Next, 0.41 g (1.74 mmol) of 4-fluorophenyl phenyl sulfone was added into the mixture. The resulting solution was stirred at 100 °C for 1.5 h. After TLC control, the mixture was cooled and quenched by the addition of ice water. The organic compounds were extracted with dichloromethane. The extract was dried by using Na_2SO_4. The final product was crystallized from methanol. Yield: 0.4 g of white material (60%). MS ($APCI^+$, 20 V): 550.12 ([M+H], 100%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.20 (d, 2H, *J* = 8.4 Hz, Ar), 8.08 (d, 2H, *J* = 8.4 Hz, Ar), 7.99 (d, 2H, *J* = 8.0 Hz, Ar), 7.92 (s, 1H, Ar), 7.78 (d, 2H, *J* = 8.4 Hz, Ar), 7.71–7.57 (m, 3H, Ar), 7.56–7.32 (m, 4H, Ar), 7.32–7.09 (m, 9H, Ar), 7.09–6.96 (m, 2H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 148.43, 142.45, 141.59, 141.37, 140.43, 139.68, 136.86, 133.50, 129.60, 129.51, 129.16, 129.04, 127.86, 126.90, 126.54, 125.64, 125.05, 123.70, 122.97, 121.93, 120.94, 120.76, 118.25, 110.56, 109.74.

4,4′-Di[3-(*N*,*N*-diphenylamino)carbazol-9-yl]benzophenone (**8**). 0.4 g (1.20 mmol) of compound **5** and 0.05 g (2.1 mmol) of 60% NaH was stirred in 10 mL of DMF under nitrogen for 30 min at room temperature. Next, 0.12 g (0.53 mmol) of 4,4′-difluorobenzophenone was added into the mixture. The formed solution was stirred for 2 h at 100 °C. After TLC tests, the mixture was cooled and quenched using ice water. The organic materials were extracted with dichloromethane. The extracts were dried using Na_2SO_4. The product was crystallized from methanol. Yield: 0.40 g of white powder (89%). MS ($APCI^+$, 20 V): 847.76 ([M+H], 100%). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.19 (d, 4H, *J* = 8.4 Hz, Ar), 8.04 (d, 2H, *J* = 7.6 Hz, Ar), 7.98 (s, 2H, Ar), 7.83 (d, 4H, *J* = 8.4 Hz, Ar), 7.68–7.37 (m, 8H, Ar), 7.34–7.22 (m, 11H, Ar), 7.22–7.05 (m, 8H, Ar), 7.04–6.97 (m, 3H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 148.50, 141.89, 141.34, 140.72, 137.21, 135.76, 131.91, 129.15, 126.47, 126.27, 125.70, 124.96, 123,630, 122.94, 121.75, 120.70, 118.36, 110.75, 109.93.

Properties of the materials are summarized in Table S1.

2.2. Preparation of OLED Devices

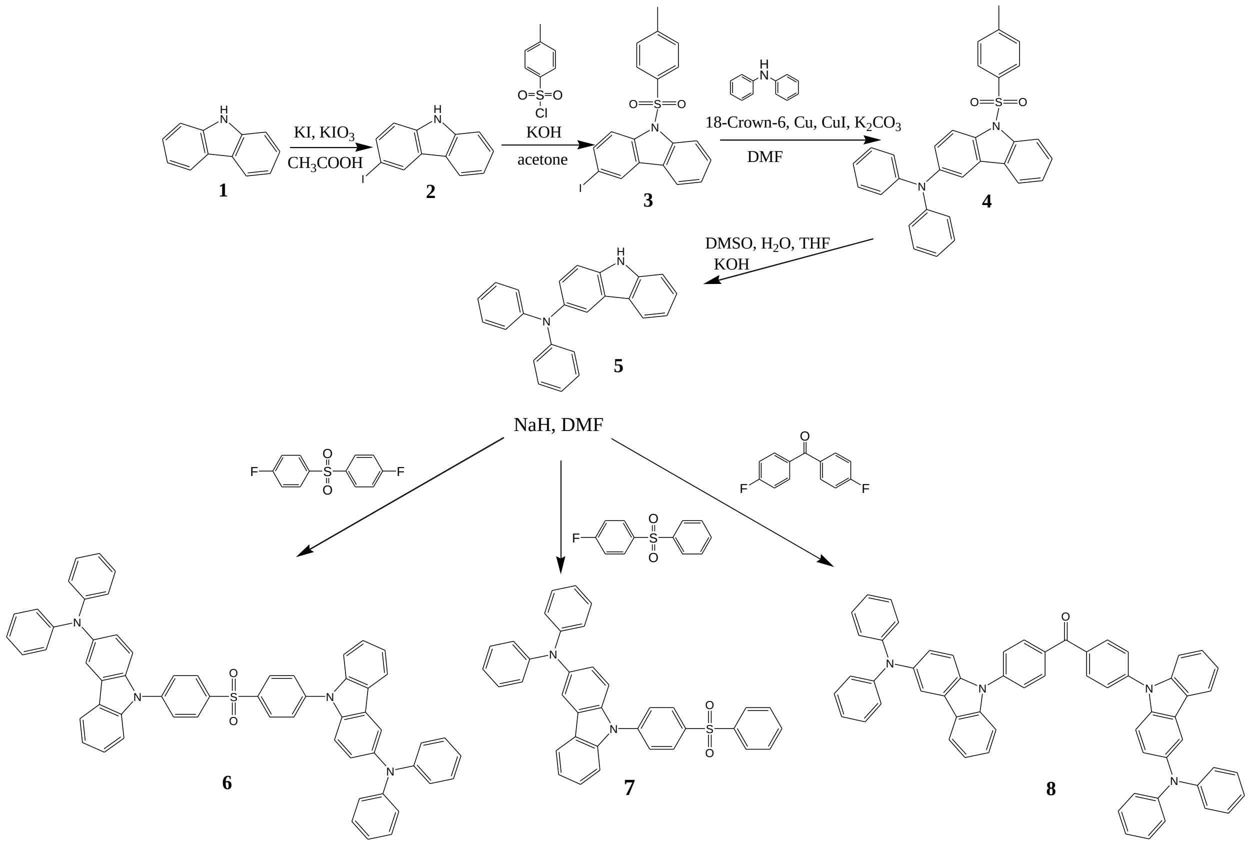
The OLEDs were formed on glass substrates and consisted of a typical structure of several organic thin films incorporated between metallic cathode and indium tin oxide (ITO, 125 nm) anode. Before use in OLEDs formation, the ITO covered substrates were carefully washed and affected with UV-ozone before formation of the organic thin films [37]. The stack of organic layers consisted of a thin film of polyethylene dioxythiophene/polystyrene sulphonate (PEDOT:PSS, 35 nm), which was used as the hole-injection layer and was prepared by spin coating [38]. It was spin-coated at 3700 rpm for 25 s to deposit the hole-injection layer on pre-cleaned ITO anode and was kept on a hot plate for heating PEDOT:PSS thin layers at 100 °C for 30 min.

Emitting layers (20 nm) in devices were formed from a mixture of host: 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) and of the synthesized emitters **6**–**7**, and were deposited by spin coating method from THF (4 mg/mL) at 2500 rpm for 20 s under nitrogen. The emitting materials were tested in concentration-dependent studies with the guest amount of 5, 10, 15, or 20 wt%.

Electron transporting 1,3,5-tris(*N*-phenylbenzimiazole-2-yl)benzene (TPBI, 40 nm) layer, electron injecting LiF (1 nm), and Al cathode (200 nm) were all formed by thermal evaporation technic in vacuum chamber with a base pressure of 4×10^{-6} Torr. The current-voltage-brightness (I-V-L) characteristics of the OLEDs was obtained by using Keithley source-measurement technic and Si photodiode, which were calibrated by using Photo Research PR-650 spectro-radiometer (Optimum Optoelectronic, GuangDong, China). Chromaticity coordinates (CIE), luminance, and electroluminescence spectra of the formed OLEDs were recorded by using the Photo Research PR-655 spectro-radiometer (Optimum Optoelectronic, GuangDong, China).

3. Results and Discussion

The synthetic route to the bipolar compounds **6–8** having 3-(*N*,*N*-diphenylamino) carbazole as an donor moiety and diphenylsulfone or benzophenone as acceptor fragment is presented in Scheme 1. A key compound, 3-(*N*,*N*-diphenylamino)-9H-carbazole (**5**), was prepared from 3-(*N*,*N*-diphenylamino)-9-tosylcarbazole (**4**) by using a multistep procedure. Firstly, 9H-carbazole (**1**) was converted to 3-iodo-9H-carbazole (**2**) by using iodination reaction of Tucker procedure. The obtained iodo-compound **2** was then used for preparation of 3-iodo-9-tosylcarbazole (**3**), which was converted to the material **4** in Ullmann reaction by using an access of *N*,*N*-diphenylamine. The objective compounds **6–8** were finally prepared in reactions of the key material **5** with, correspondingly, bis(4-fluorophenyl)sulfone, 4-fluorophenylsulfone, and 4,4′-difluorobenzophenone. All the newly prepared derivatives were characterized by mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy.



Scheme 1. Synthetic pathway of the objective materials **6**–**8**.

The behaviour for heating of the prepared objective derivatives **6–8** was tested by using TGA (thermo-gravimetric analysis) and DSC (differential scanning calorimetry) under a nitrogen atmosphere. It has been demonstrated that the materials have very high thermal stabilities. The values of temperatures of 5% weight loss (T_{ID}) for the derivatives were 389 °C for **6**, 398 °C for **8**, and 351 °C for **7**, as it was confirmed by the TGA method by using the heating rate of 10 $°C \cdot min^{-1}$. TGA curve of the compound **7** is shown in Figure 1 as an example. The curves of other objective derivatives are presented in electronic Supporting Information (Figures S1 and S2). The highest thermal stability was observed for the derivatives **6** and **8**, which have the higher molecular weight. It could be seen that thermal stabilities of the materials prepared increase with the increase of their molecular weight (cf. T_{ID} of **6** and **8** with that of **7**).

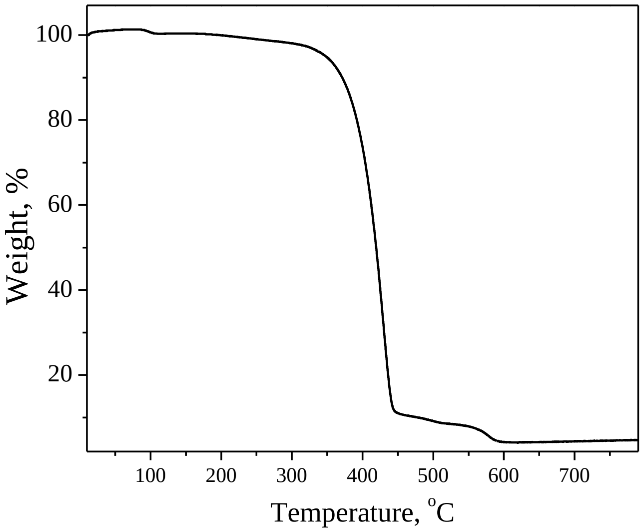


Figure 1. TGA curve of compound **7**. Heating rate: 10 °C min^{-1}.

All the derivatives **6**–**8** were obtained after chromatographic purification as amorphous materials with very high values of the glass transition temperatures, as demonstrated by the method of DSC. When specimens of the derivatives **6**–**8** were heated during the DSC experiment, only T_gs were observed correspondingly at 111 °C for **7**, at 159 °C for **8**, and at 173 °C for **6**, and no peaks due to crystallization and melting appeared during the further heating and cooling scans. The DSC thermo-grams of the second heating of the compounds **6**–**8** are shown in Figure 2.

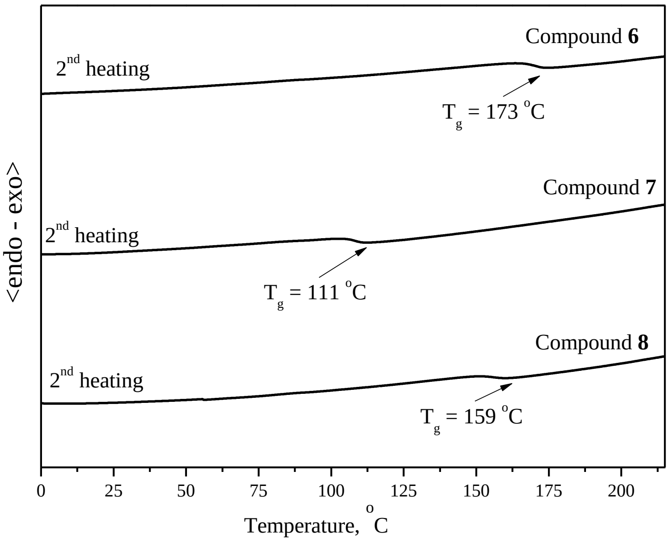


Figure 2. DSC curves of second heating of the materials **6**–**8**. Heating rate: 10 °C·min^{-1}.

The comparison of values of the T_gs demonstrates that an increase in molecular weight of the derivatives leads to the increase of value of T_g. For example, T_g of dimers **6** and **8** are 49–62 °C higher than that of compound **7**, having just one 3-(*N*,*N*-diphenylamino)carbazole fragment. The high thermal stabilities and high T_gs of the electroactive compounds show their good potential for the formation of thin and thermally stable homogenous films that are well-suited for application in OLEDs.

Compounds **6** and **7**, having the best solubility and suitable for preparation of layers by spin-coating, were tested as emitters dispersed in CBP host for the OLEDs. The emitting materials were tested in concentration-dependent tests with an amount of the guest of 5, 10, 15, or 20 wt%. Structures of the OLEDs are presented in the Experimental part. When the devices ITO/ PEDT:PSS/emitter **7** in CBP/TPBI/LiF/Al were fabricated and tested, blue emissions with maxima around 456 nm and (0.17, 0.21) International Commission on Illumination (CIE) coordinates were obtained at brightness of 100 cd/m^2, as it is presented in Figure 3 as an example. These emissions overlap with the emission of **7** pure layer. This confirms that recombination of charges occurs in the emitting thin film of **7** dispersed in CBP. Low operation voltages with brightness of 100 cd/m^2 at 5.0–5.5 V were characteristic for the devices. The device fabricated using 5 wt% of the emitter demonstrated the best performance with a current efficiency of 1.9 cd/A, power efficiency of 1.2 lm/W, and EQE exceeding 1.3% at 100 cd/m^2, as well as a maximum luminance of 1005 cd/m^2. The rather low efficiencies suggest poor confinement of carriers and excitons in the devices, and/or poor balance of hole and electron currents.

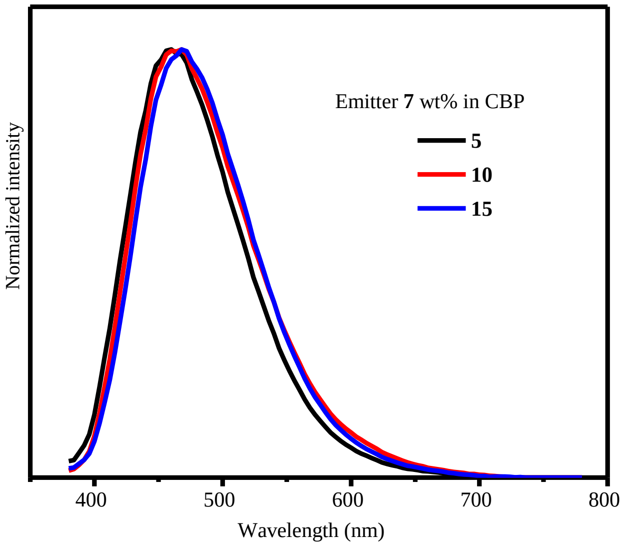


Figure 3. Emission spectra of OLEDs using emitter **7** in CBP host.

The same hetero-structure devices: ITO/PEDOT:PSS/emitter **6** in CBP/TPBI/LiF/Al employing **6** as the emitter in combination with CBP host were then also investigated in concentration-dependent experiments. It has been established that, in this configuration, the charge recombination also occurred in the layers of **6** dispersed in CBP (Figure S3). Figure 4 shows current—voltage and luminance—voltage characteristics as well as EQE of the devices. The rather low turn-on voltages of 3.0–3.5 V, measured as the voltages where light emission was detectable, and low voltages of the operation (100 cd/m^2 at 5.0–5.5 V) of these OLEDs, demonstrated that the bipolar derivatives can function well as the emitters.

The devices with quest **6** also showed maximum brightness of 2442–3160 cd/m^2, current efficiencies of 2.5–3.2 cd/A, power efficiencies of 1.6–2.2 lm/W, and external quantum efficiencies (EQE) of 1.5%–1.7% at 100 cd/m^2. The device containing 15 wt% of the guest **6** demonstrated the best overall characteristics, with maximum luminance exceeding 2630 cd/m^2, current efficiency of 3.2 cd/A, power efficiency of 2.2 lm/W, and EQE exceeding 1.7% at 100 cd/m^2. The efficiencies of the OLEDs had only a small drop in the observed luminance window, for the technically important brightness of 1000 cd/m^2 efficiencies above 2.5 cd/A (1.4%) have been obtained.

The characteristics of all the devices are summarized in Table S2. It should be emphasized that these efficiencies have been measured in non-optimized test OLEDs and under simple laboratory conditions and should not be compared with efficient and optimized blue OLEDs, which are presented at the moment in literature [39–41]. Characteristics of the OLEDs could be improved by an optimization of the thin films' thicknesses and processing technology.

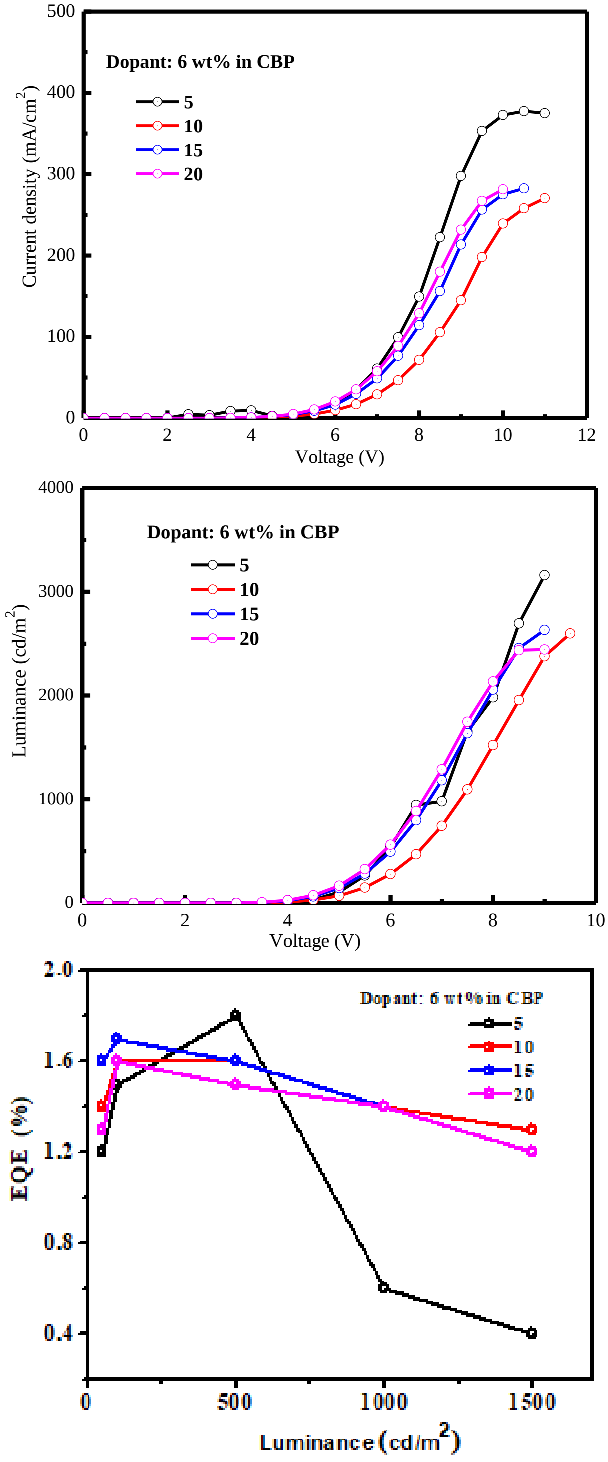


Figure 4. OLED characteristics of the multilayer devices: ITO/PEDT/emitter **6** in CBP/TPBI/LiF/Al.

In conclusion, novel electro-active bipolar derivatives have been prepared using 3-(*N*,*N*-diphenylamino)carbazole as electron donor fragment connected with various electron acceptors. The derivatives can form homogeneous solid amorphous layers with very high glass transition temperatures of 111–173 °C. The materials, which were well soluble in common organic solvents, were tested as emitting materials dispersed in 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) host. The OLED with the emitter bis[4-{3-(*N*,*N*-diphenylamino)carbazol-9-yl}phenyl] sulfone exhibited the best overall performance. The OLED using the emitter demonstrated low turn-on voltage of 3.0 V, maximum brightness exceeding 2630 cd/m^2, current efficiency of 3.2 cd/A, power efficiency of 2.2 lm/W, and

EQE exceeding 1.7% at 100 cd/m^2. For the technically important brightness of 1000 cd/m^2, efficiencies above 2.5 cd/A (1.4%) were obtained. The results demonstrate that some of the materials could be further investigated as potential TADF emitters.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings12070932/s1, Figure S1: TGA curve of compound **6**. Heating rate: 10 °C min^{-1}; Figure S2: TGA curve of compound **8**. Heating rate: 10 °C min^{-1}; Figure S3: Emission spectra of OLEDs using emitter **6** in CBP host; Table S1: Photophysical, thermal, and electrochemical characteristics of the objective derivatives **6**–**8**; Table S2: Summarized electroluminescent properties of the described OLEDs.

Author Contributions: Methodology, D.T.; software, D.B.; investigation, R.B.; resources, G.J.; data curation, G.K.; writing—original draft preparation, S.S.S.; writing—review and editing, S.G.; supervision, J.-H.J.; project administration, D.T.; funding acquisition, S.G. All authors have read and agreed to the published version of the manuscript.

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