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RESEARCH-ARTICLE



Oligomers containing pyridinyl-substituted carbazole rings as host materials for phosphorescent OLEDs

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ABSTRACT

Two oligoethers containing electroactive pendent pyridinyl-carbazole moieties have been synthesized by the multi-step synthetic route. Full characterization of their structures is presented. The oligomers represent derivatives of very high thermal stability with initial thermal degradation temperatures exceeding 400 °C. Glass transition temperatures of the amorphous materials were also very high and reached values of 124 °C and 145 °C, respectively. Bipolar chemical structure having oligomer, i.e. poly{3-(2-methoxy-3-pyridinyl)-9-(3-methyloxetan-3-yl)methyl-carbazole} was tested as host material for green phosphorescent organic light emitting diode using tris(2-phenylpyridine)iridium(III) as a triplet emitter. A green device containing 10 wt% of the green guest demonstrated among all the devices the best performance with current efficiency of 8.8 cd/A and power efficiency of 5.1 lm/W at 100 cd/m². At higher brightness, such as 1000 cd/m², used for illumination applications, this PhOLED showed enhanced efficiency of 11.7 cd/A (5.4 lm/W) with brightness exceeding 4000 cd/m².

KEYWORDS

Carbazole derivative; oligomer; thermal stability; organic light emitting diode

1. Introduction

Organic light emitting diode (OLED) is a potential technology to realize high quality displays and solid state lightings [1, 2]. Nowadays, wide range of OLED based portable display products and few large size displays have already been in the market [3, 4]. The efficiencies of the devices have advanced rapidly in recent years because of the development of efficient phosphorescent guests. In phosphor-doped OLEDs (PhOLEDs), to reduce quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet-triplet annihilation etc., the triplet emitters of heavy-metal complexes are normally used as emitting guests in a host material, and thus suitable host materials are of equal importance for the phosphorescent devices [5–7]. For electrophosphorescence from triplet guests, it is essential that the triplet level of the host is larger than that of the triplet emitter to prevent reverse energy transfer from the guest back to the host and to effectively confine triplet excitons on guest molecules [8–10].

It was reported earlier that carbazole-based derivatives demonstrate rather large triplet energies and are potential host materials for blue electrophosphorescent devices

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[11–15]. The derivatives are also used as hole transporting materials and emitters [16–21]. Here, we report on bipolar solution process-able host materials containing electroactive pendent pyridinyl-carbazole moieties.

2. Experimental

2.1. Instrumentation

^1H NMR spectra were recorded using a Varian Unity Inova (300 MHz) apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

The PhOLEDs were fabricated on glass substrates and consisted of multiple organic layers sandwiched between the bottom indium tin oxide (ITO) anode and the top metal cathode (Al). The device structure used was ITO/PEDOT:PSS (ca. 30 nm)/new oligomeric host doped with $\text{Ir}(\text{ppy})_3$ /LiF (0.5 nm)/Al (150 nm), where the conducting polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was used as the hole-injection layer [22], the oligomeric host 7 doped with the green phosphorescent tris(2-phenylpyridine)iridium(III) ($\text{Ir}(\text{ppy})_3$) was used as the emitting layers (~ 40 nm), and LiF was used as the electron-injecting layer for the devices [23]. All the emitting layers were prepared by spin coating from solutions. Thickness of the layers was controlled by changing speed (rpm) of the substrate. The layers of LiF and of Al cathode were then deposited at 1×10^{-5} torr.

The luminance and CIE chromatic coordinates of the resulting OLEDs were measured using a Minolta CS-100 luminance meter. A Keithley 2400 electrometer was used to measure the current-voltage (I-V) characteristics. All the devices were characterized without encapsulation and all the measurements were carried out under ambient condition. The emission area of all the devices was 25 mm^2 and only the luminance in the forward direction was measured.

2.2. Materials

9H-Carbazole (**1**), 3-bromomethyl-3-methyloxetane, 6-methoxy-3-pyridinylboronic acid, 2-methoxy-3-pyridinylboronic acid, bis(triphenylphosphine)palladium(II) dichloride [$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$], boron trifluoride diethyl etherate [$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$], tetra-N-butylammonium bromide, Na_2SO_4 and KOH were purchased from Aldrich and used as received.

3-Iodo-9H-carbazole (**2**) [24] and 3-iodo-9-(3-methyloxetan-3-yl)methylcarbazole (**3**) [25] were synthesized according to the procedures outlined in literature.

3-(6-Methoxy-3-pyridinyl)-9-(3-methyloxetan-3-yl)methylcarbazole (**4**). 1.4g (3.7mmol) of 3-iodo-9-(3-methyloxetan-3-yl)methylcarbazole (**3**), 1g (6.6mmol) of 6-methoxy-3-pyridinylboronic acid, 0.14g (0.19mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$ and 1.4g (24.9mmol) of powdered potassium hydroxide were stirred in 20 ml of THF containing degassed water (1.5 ml) at 80°C under nitrogen for 24 h. After TLC control the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethylacetate. The combined extract was dried over anhydrous Na_2SO_4 . The crude product was purified by

silica gel column chromatography using the mixture of ethylacetate and hexane (vol. ratio 1:3) as an eluent. Yield: 0.8 g of yellowish crystals. M.p.: 134 °C (DSC).

MS (APCI⁺, 20 V): 359.1 ([M + H], 100%). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.48 (d, 1H, *J* = 1.8 Hz Ar), 8.22 (d, 1H, *J* = 2.1 Hz Ar), 8.14 (d, 1H, *J* = 7.2 Hz Ar), 7.90 (dd, 1H, *J*₁ = 2.4 Hz, *J*₂ = 8.7 Hz Ar), 7.61 (dd, 1H, *J*₁ = 1.8 Hz, *J*₂ = 8.7 Hz Ar), 7.52–7.38 (m, 4H, Ar), 7.35–7.23 (m, 1H, Ar), 4.80 (d, 2H, *J* = 6.0 Hz, CH₂ of oxetanyl fragment), 4.47 (s, 2H, NCH₂), 4.38 (d, 2H, *J* = 6.0 Hz, CH₂ of oxetanyl fragment), 4.01 (s, 3H, OCH₃), 1.47 (s, 3H, CH₃).

3-(2-Methoxy-3-pyridinyl)-9-(3-methyloxetan-3-yl)methylcarbazole (5). 1g (2.6 mmol) of 3-iodo-9-(3-methyloxetan-3-yl)methylcarbazole (3), 0.8g (5.3 mmol) of 2-methoxy-3-pyridinylboronic acid, 0.07g (0.101 mmol) of PdCl₂(PPh₃)₂ and 0.7g (11 mmol) of powdered potassium hydroxide were stirred in 20 ml of THF containing degassed water (1.5 ml) at 80 °C under nitrogen for 24 h. After TLC control the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethylacetate. The combined extract was dried over anhydrous Na₂SO₄. The crude product was purified by silica gel column chromatography using the mixture of ethylacetate and hexane (vol. ratio 1:2) as an eluent. Yield: 0.72 g of rosy crystals. M.p.: 117 °C (DSC).

MS (APCI⁺, 20 V): 359.1 ([M + H], 100%). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.26 (d, 1H, *J* = 1.8 Hz Ar), 8.17 (dd, 1H, *J*₁ = 1.2 Hz, *J*₂ = 4.8 Hz Ar), 8.12 (d, 1H, *J* = 8.1 Hz Ar), 7.65–7.63 (m, 2H, Ar), 7.50–7.36 (m, 3H, Ar), 7.29–7.22 (m, 1H, Ar), 7.00 (dd, 1H, *J*₁ = 5.1 Hz, *J*₂ = 7.2 Hz Ar), 4.80 (d, 2H, *J* = 6.0 Hz, CH₂ of oxetanyl fragment), 4.47 (s, 2H, NCH₂), 4.38 (d, 2H, *J* = 6.0 Hz, CH₂ of oxetanyl fragment), 4.01 (s, 3H, OCH₃), 1.47 (s, 3H, CH₃).

Poly{3-(6-methoxy-3-pyridinyl)-9-(3-methyloxetan-3-yl)methylcarbazole} (6). Monomer 4 (0.7g, 1.95 mmol) was polymerized in 3.9 ml of 1,2-dichloroethane by using 8.3 mg (0.058 mmol) of BF₃·O(C₂H₅)₂ as an initiator. Polymerization mixture was stirred at 60 °C under nitrogen for 24 h. After precipitation into methanol, the low molecular weight fractions of the polymer were removed by Soxhlet extraction of the raw material with methanol. Yield: 0.3 g (42%) of yellowish amorphous powder. GPC: *M*_w = 1100, *M*_n = 860. ¹H NMR (400 MHz, CDCl₃, δ, m.d.): 8.52–6.78 (m, 10H, Ar); 4.83–3.40 (m, 9H, NCH₂ ir CH₂OCH₂ ir OCH₃), 1.68–0.81 (m, 3H, CH₃).

Poly{3-(2-methoxy-3-pyridinyl)-9-(3-methyloxetan-3-yl)methylcarbazole} (7). Monomer 5 (0.5g 1.38 mmol) was polymerized in 2.7 ml of 1,2-dichloroethane by using 5.9 mg (0.042 mmol) of BF₃·O(C₂H₅)₂ as an initiator. Polymerization mixture was stirred at 60 °C under nitrogen for 24 h. After precipitation into methanol, the low molecular weight fractions of the polymer were removed by Soxhlet extraction of the raw material with methanol. Yield: 0.3 g (42%) of white amorphous powder. GPC: *M*_w = 6350, *M*_n = 1920. ¹H NMR (400 MHz, CDCl₃, δ, m.d.): 8.23–6.71 (m, 10H, Ar); 4.40–3.15 (m, 9H, NCH₂ ir CH₂OCH₂ ir OCH₃), 1.24–0.73 (m, 3H, CH₃).

3. Results and discussion

Synthesis of the oligoethers (4–5) was carried out by a multi-step synthetic route as shown in Figure 1. 3-Iodo-9H-carbazole (2) as a key material was synthesized from

Table 1. Molecular weights and PDI of oligomers **6** and **7**

Polymer	M_w	M_n	PDI	T_g
6	860	1100	1.28	124
7	1920	635	3.31	145

commercially available 9H-carbazole (**1**) by Tucker iodination procedure. The iodo-derivative **2** was converted to oxetanyl-functionalized compound **3** by reaction with large excess of 3-bromomethyl-3-methyloxetane under basic conditions in the presence of a phase transfer catalyst. The monomers **4** and **5** were then obtained from 3-iodo-9-(3-methyloxetan-3-ylmethyl)carbazole by its Suzuki reaction with 6-methoxy-3-pyridinylboronic acid or 2-methoxy-3-pyridinylboronic acid, correspondingly. Oligomers **6** and **7** were prepared by cationic polymerization of the corresponding monomers **4** or **5** in 1,2-dichloroethane solutions using $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ as an initiator. Low-molecular-weight fractions of the products of polymerizations were removed by Soxhlet extraction of the raw polymers with methanol.

The newly synthesized derivatives were identified by mass spectrometry (low molar mass derivatives) and NMR spectroscopy (oligomers). The data were found to be in good agreement with the proposed structures. Oligomers **6** and **7** were soluble in common organic solvents, such as chloroform and THF at room temperature. Transparent thin films of these materials could be prepared by spin coating from their solutions.

The number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity indexes (PDI) of these oligomers were estimated by GPC. The data are presented in the Table 1. It was observed that low-molecular-weight oligomers, i.e. oligomers were obtained after the cationic polymerization. It should be mentioned that molecular weights of the oligomers **6** and **7** are very close to those of the earlier described polyethers containing unsubstituted carbazole rings [26].

The behaviour under heating of the materials **6** and **7** was studied by DSC and TGA under a nitrogen atmosphere. DSC measurements confirmed that the synthesized oligomers are amorphous materials with high glass transition temperatures (T_g), which are desirable for application of the electroactive materials in OLEDs. When sample of oligomer **6** was heated, glass transition was observed at 124 °C and no peaks due to crystallisation and melting appeared in the range from -30 °C to 220 °C. When the sample was cooled, it formed again the amorphous material with T_g of 124 °C. The sample of oligomer **7** demonstrated analogous behaviour during the DSC experiment. Its glass transition was observed at 145 °C and no peaks due to crystallisation and melting appeared in the range from -30 °C to 220 °C.

The oligomers demonstrated rather high thermal stability during the TGA experiment as it could be seen from Figure 2 as an example. The temperature at 5% weight loss (T_{ID}) of oligomer **7** was 412 °C indicating good thermal stability of the material. The sample of oligomer **6** demonstrated similar behaviour during the DSC experiment. Its T_{ID} was exceeded 400 °C.

To evaluate the performance of the new electroactive oligomers as host materials, phosphorescent green OLEDs were fabricated using green triplet emitter $\text{Ir}(\text{ppy})_3$ as the guest. The structure of the multilayer devices was ITO/PEDOT:PSS/oligomeric host **7**

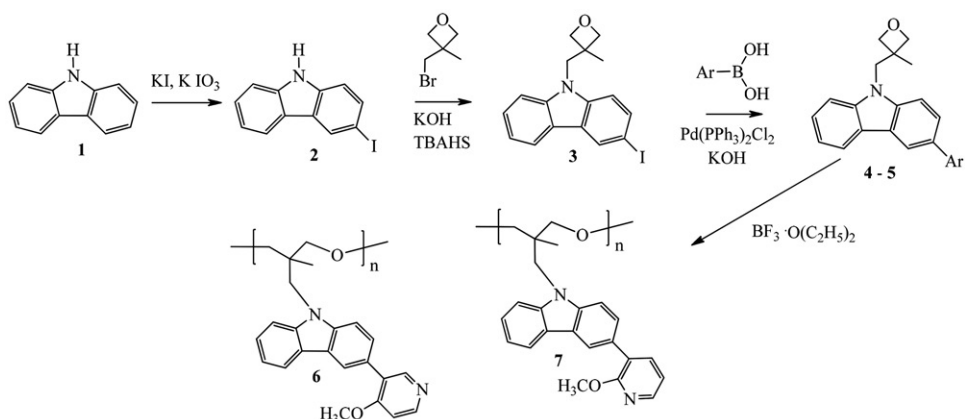


Figure 1. Synthetic pathway of the electroactive oligomers.

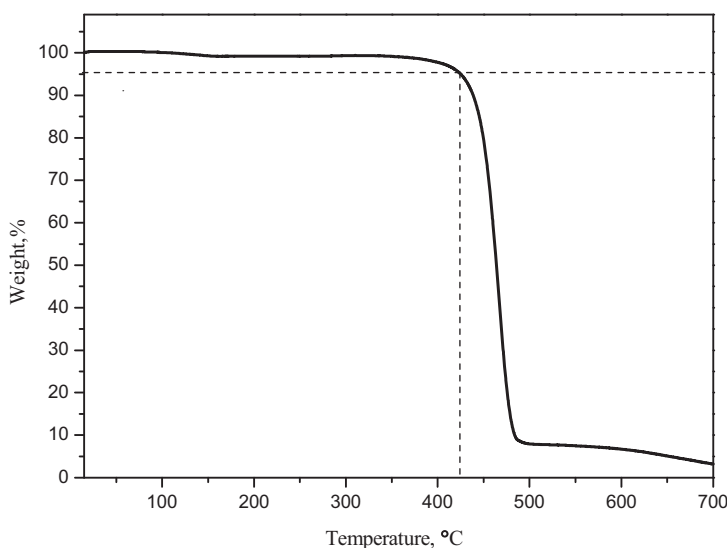


Figure 2. TGA curve of the oligomer 7. Heating rate: 10 °C/min.

doped with $\text{Ir}(\text{ppy})_3/\text{LiF}/\text{Al}$. Details of fabrication of the devices are described in Experimental part.

The oligomer 7 demonstrated better film forming properties as well as compatibility with $\text{Ir}(\text{ppy})_3$ guest. It was used in concentration-dependent PhOLED experiments with the green guest amount ranging from 7 to 15 wt%. The electro-phosphorescence was found to originate only from $\text{Ir}(\text{ppy})_3$ at different bias voltages in all these devices as it is demonstrated in Figure 3. No host and doped transport molecular emission was visible from the OLEDs, indicating an energy transfer or charge transfer from the host to the guest as well as the sufficient injection of both holes and electrons into the emitting layer.

Figure 4 shows characteristics of the devices. These PhOLEDs exhibited rather low turn-on voltages of 4.0 – 5.1 V, maximal current efficiencies of 12.2 – 14.9 cd/A, maximal power efficiencies of 6.1 – 7.3 lm/W and maximal brightness of 3500–4073 cd/m².

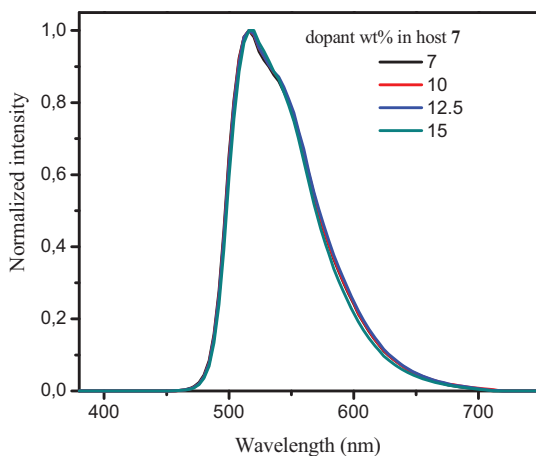


Figure 3. Electro-phosphorescent spectra of PhOLEDs with the green guest amount ranging from 7 to 15 wt%.

Efficiency roll-off at higher currents, which is typical for phosphorescent OLEDs, was also observed here; however at high brightness of 1000 cd/m^2 current efficiencies of $11.0 - 11.9 \text{ cd/A}$ and maximal power efficiencies of $4.9 - 5.6 \text{ lm/W}$ were still obtained. It could be observed that rather high efficiencies of $6.8 - 7.3 \text{ cd/A}$ ($2.3 - 2.8 \text{ lm/W}$) were established even at very high brightness of 3000 cd/m^2 .

A green device containing 10 wt% of **Ir(ppy)₃** guest exhibited among all the devices the best performance with current efficiency of 8.8 cd/A and power efficiency of 5.1 lm/W at 100 cd/m^2 . At higher brightness, such as 1000 cd/m^2 , used for illumination applications, this PhOLED showed even enhanced efficiency of 11.7 cd/A (5.4 lm/W). Maximal brightness of the device exceeded 4000 cd/m^2 at 10 V.

In conclusion, new oligoethers with pyridinyl-carbazole electroactive units have been synthesized by cationic polymerization of the corresponding oxetane-based monomers. The amorphous oligomers have high thermal stability as well as very high glass transition temperatures (124°C and 145°C) and are expected to show also high morphological stability of thin electroactive films. Better film forming properties and compatibility with triplet emitter of tris(2-phenylpyridine)iridium(III) (**Ir(ppy)₃**) having bipolar polymer was tested as host material for green phosphorescent organic light emitting diode. The host was used in concentration-dependent PhOLED experiments with the green guest amount ranging from 7 to 15 wt%. A green device containing 10 wt% of **Ir(ppy)₃** guest demonstrated among all the devices the best performance with current efficiency of 8.8 cd/A and power efficiency of 5.1 lm/W at 100 cd/m^2 . At higher brightness, such as 1000 cd/m^2 , used for illumination applications, this PhOLED showed enhanced efficiency of 11.7 cd/A (5.4 lm/W). Maximal brightness of the device exceeded 4000 cd/m^2 at 10 V.

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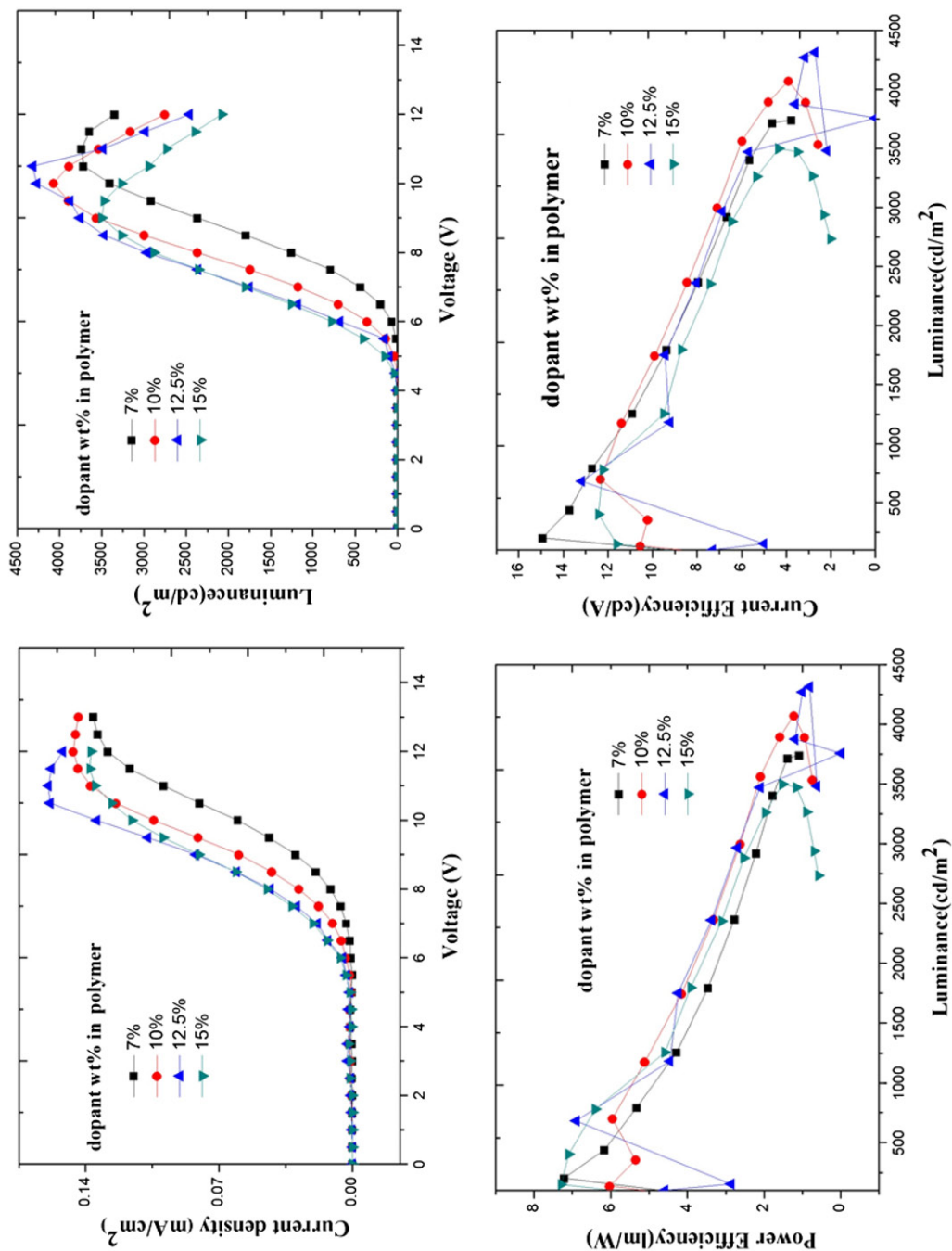


Figure 4. OLED characteristics of the devices with the configuration: ITO/PEDOT:PSS/oligomeric host 7 doped with Ir(ppy)₃/LiF/Al.

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