Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: D. Tavgeniene, G. Krucaite, L. Peciulyte, G. Buika, E. Zaleckas, F. Dumur & S. Grigalevicius (2016) New carbazole-indan-1,3-dione- based host materials for phosphorescent organic light emitting diodes, Molecular Crystals and Liquid Crystals, 640:1, 145-151, DOI: 10.1080/15421406.2016.1257320

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1257320

Published online: 14 Dec 2016.

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 640, 145–151
http://dx.doi.org/10.1080/15421406.2016.1257320

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New carbazole-indan-1,3-dione- based host materials for phosphorescent organic light emitting diodes

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ABSTRACT

New carbazole- and indan-1,3-dione -based low molecular weight derivatives were synthesized and characterized by mass spectrometry and ^{1}H NMR spectroscopy. Thermal behaviour of the derivatives was demonstrated by thermo-gravimetric analysis and differential scanning calorimetry. The materials were found to show very high thermal stability having initial thermal degradation temperatures in the range of 398- 401°C. Glass transition temperatures of the amorphous molecular materials were in the rage of 80–114°C. The derivatives were tested as host materials in blue phosphorescent organic light emitting diodes with iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N,C2'*]picolinate as the guests. One of the blue OLED devices demonstrated rather low turn-on voltage of 5.0 V, a maximum luminance efficiency of 2.73 cd/A and maximum brightness of about 220 cd/m^2.

KEYWORDS

carbazole; indandione; amorphous layer; host material; light emitting diode

1. Introduction

Triplet emitters are normally used as emitting guests in host materials in phosphorescent organic light emitting diodes (PhOLEDs), to reduce quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet-triplet annihilation etc. New hosts are recently widely synthesized and investigated for the phosphorescent devices [1, 2, 3, 4]. For electro-phosphorescence from triplet guests, it is important that the triplet level of the host would be 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[5, 6, 7, 8]. The host materials for blue electro-phosphorescence reported thus far are limited to a few functionalities, including carbazoles and phenylsilanes; however, only carbazole-based materials simultaneously possess sufficiently large triplet energies and carrier transport properties[9, 10, 11, 12, 13, 14]. Another essential requirement for the successful operation of the devices is the ability of the material to form stable amorphous films[15]. We have synthesized and described here branched mono-disperse derivatives containing electron donating as well as electron accepting chromophores as bipolar host materials for electro-phosphorescent layers. The derivatives could be purified by column chromatography. They demonstrated stable

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amorphous states and easy process-ability of electro-phosphorescent layers by spin-coating techniques.

2. Experimental

2.1. Instrumentation

^{1}H 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 TGAQ50 aparatus. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10° C/min.

The devices 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. 40 nm)/new host doped with **FIrpic**/TPBi (50 nm)/LiF (1 nm)/Al (150 nm), where the conducting polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was used as the hole-injection layer [16], the synthesized hosts **5** and **6** doped with blue phosphorescent iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N,C2′*]picolinate (**FIrpic**) were used as the emitting layers (∼40 nm), 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBi) was used as an electron-transporting layer and LiF was used as the electron-injecting layer for the devices[17]. All the emitting layers were prepared by spin coating from solutions. The layers of TPBi and of LiF as well as Al cathode were then deposited at 1×10^{-5} torr.

External Quantum Efficiency Measurement System (model C9920-12) of Hamamatsu Photonics K.K. was used to measure the current-voltage-luminance characteristics of the OLED devices. All the OLEDs were characterized without encapsulation and all the measurements were carried out under ambient condition.

2.2. Materials

9H-Carbazole (**1**), potassium hydroxide (KOH), phosphorus trichloride ($POCl_3$), dimethylformamide (DMF), indan-1,3-dione, 1,4-dioxane and ethanol were purchased from Aldrich and used as received.

1,6-di(9-carbazolyl)hexane (**2**) was prepared by procedure described in the literature[18].

3-Formyl-9-[6-(9-carbazolyl)hexyl]carbazole (**3**) was prepared by the reaction of compound **2** with $POCl_3$ in DMF by Vilsmeier procedure[19]. $POCl_3$ (4.6 g, 30 mmol) was added dropwise to dry DMF (3 ml) at 0 °C under nitrogen atmosphere. 1,6-di(9-carbazolyl)hexane (**2**) (2 g, 4.8 mmol) was dissolved in dichloromethane and poured to the mixture of DMF and $POCl_3$. The resulting mixture was stirred at 80 °C for 6 h, until the starting compound **2** reacted completely. Then the mixture was cooled down to the room temperature, poured into ice water and neutralized with sodium acetate till pH 6–8. The resulting mixture was extracted by chloroform. Organic fraction was dried by $NaSO_4$ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:3) as an eluent. Yield of the product (**3**) was 1.8 g (85%). MS (APCI+, 20 V): 445.22 ([M + H], 100%). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 10.08 (s, 1H, ArC<u>H</u>O), 8.59 (s, 1H, Ar), 8.16–7.94 (m, 4H, Ar), 7.52–7.19 (m, 10H, Ar), 4.26 (t, 4H, J = 6.9 Hz, 2×NCH_2), 1.88–1.79 (m, 4H, 2×$NCH_2C\underline{H}_2$), 1.41–1.33 (m, 4H, 2×$NCH_2CH_2C\underline{H}_2$).

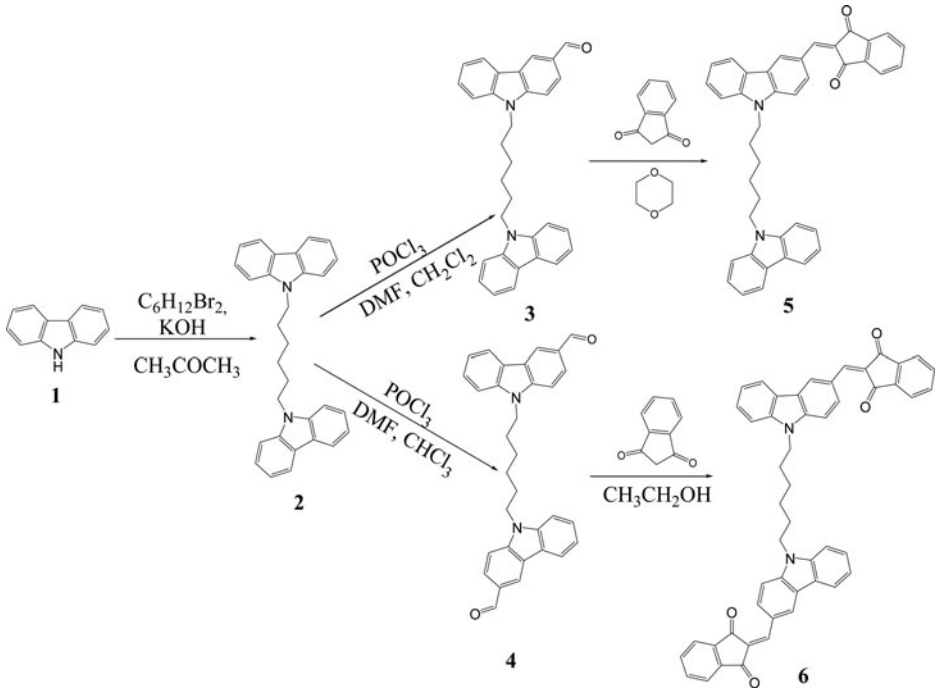
1,6-di-(3-formylcabazol-9-yl)hexane (**4**) was prepared by the reaction of compound **2** with mixture of $POCl_3$ and DMF by Vilsmeier procedure [18]. $POCl_3$ (9.2 g, 60 mmol) was added dropwise to 6 ml of dry DMF at 0 °C under nitrogen atmosphere. 1,6-di(9-carbazolyl)hexane (**2**) (2 g, 4.8 mmol) was dissolved in chloroform and poured to the mixture of DMF and $POCl_3$. The resulting mixture was stirred at 80 °C for 48 h, until the starting compound **2** reacted completely. Then the mixture was cooled down to the room temperature, poured into ice water and neutralized with sodium acetate till pH 6–8. The resulting mixture was extracted by chloroform. Organic fraction was dried by $NaSO_4$ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:3) as an eluent. Yield of the product (**4**) was 1.9 g (84%). MS (APCI+, 20 V): 473.23 ([M + H], 100%). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 10.11 (s, 2H, 2×ArCHO), 8.62 (s, 2H, Ar), 8.16 (d, 2H, J = 8.0 Hz, Ar), 7.98 (dd, 2H, J_1 = 1.6 Hz, J_2 = 8.4 Hz, Ar), 7.59–7.42 (m, 2H, Ar), 7.43–7.31 (m, 6H, Ar), 4.30 (tr, 2H, J = 6.8 Hz, 2×NC$\underline{H}_2$), 1.91–1.82 (m, 4H, 2×NCH$_2$C$\underline{H}_2$), 1.43–1.35 (m, 4H, 2×NCH$_2$CH$_2$C$\underline{H}_2$).

3-(1,3-dioxoindan-2-ylmethylene)-9-[6-(carbazol-9-yl)hexyl]carbazole (**5**) was prepared by the reaction of compound **3** with excess of indan-1,3-dione in 1,4-dioxane. 3-Formyl-9-[6-(9-carbazolyl)hexyl]carbazole (**5**) (1 g, 2.25 mmol) and indan-1,3-dione (0.6 g, 4.1 mmol) were stirred in 15 ml of 1,4-dioxane at room temperature for 12 h. Then the mixture was poured into ice water and neutralized with sodium acetate till pH 6–8. The resulting mixture that had been formed was filtered off, washed with ethanol and dissolved in chloroform. Organic fraction was dried by $NaSO_4$ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:10) as an eluent. Yield: 0.7 g (54%) of yellow crystals. M.p.: 188°C (DSC). %). MS (APCI+, 20 V): 573.3 ([M + H], 100%). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 9.44 (s, 1H, CH), 8.59 (dd, 1H, J_1 = 1.6 Hz, J_2 = 8.8 Hz, Ar), 8.24–8.15 (m, 1H, Ar), 8.11–7.92 (m, 5H, Ar), 7.81–7.71 (m, 2H, Ar), 7.48–7.27 (m, 8H, Ar), 7.22–7.16 (m, 3H, Ar), 4.23 (tr, 4H, J = 6.8 Hz, 2×NC$\underline{H}_2$), 1.88–1.73 (m, 4H, 2×NCH$_2$C$\underline{H}_2$), 1.40–1.29 (m, 4H, 2×NCH$_2$CH$_2$C$\underline{H}_2$).

1,6-di-[3-(1,3-dioxoindan-2-yl-methylene)carbazol-9-yl)hexane (**6**) was prepared by the reaction of compound **4** with excess of indan-1,3-dione in ethanol. 1,6-di-(3-formylcabazol-9-yl)hexane (**4**) (1 g, 2.12 mmol) and indan-1,3-dione (0.9 g, 6.3 mmol) were stirred in 25 ml of ethanol at room temperature overnight. Then the mixture was poured into ice water and neutralized with sodium acetate till pH 6–8. The resulting mixture that had been formed was filtered off, washed with ethanol and dissolved in chloroform. Organic fraction was dried by $NaSO_4$ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:5) as an eluent. Yield: 0.8 g (52%) of yellow crystals. M.p.: 275°C (DSC). MS (APCI+, 20 V): 751.4 ([M + Na], 100%). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 9.38 (s, 2H, 2×CH), 8.57 (dd, 2H, J_1 = 1.4 Hz, J_2 = 9.0 Hz, Ar), 8.06–8.01 (m, 2H, Ar), 7.97–7.89 (m, 4H, Ar), 7.76–7.67 (m, 4H, Ar), 7.45–7.39 (m, 2H, Ar), 7.33–7.25 (m, 6H, Ar), 4.22 (tr, 4H, J = 7.0 Hz, 2×NC$\underline{H}_2$), 1.82–1.75 (m, 4H, 2×NCH$_2$C$\underline{H}_2$), 1.34–1.29 (m, 4H, 2×NCH$_2$CH$_2$C$\underline{H}_2$).

3. Results and discussion

The synthesis of indan-1,3-dione-carbazole-based host materials (**5–6**) was carried out by a multi-step synthetic route as shown in Scheme 1. 1,6-Di-(9-carbazolyl)hexane (**2**) as the key starting material was synthesized by reaction of carbazole (**1**) with 1,6-dibromhexane under basic conditions in acetone. 3-Formyl-9-[6-(9-carbazolyl)hexyl]carbazole (**3**) and 1,6-di-(3-formylcarbazol-9-yl)hexane (**4**) were prepared from the twin compound **2** by the Vilsmeier



Scheme 1.

procedure. 3-(1,3-dioxoindan-2-ylmethylene)-9-[6-(carbazol-9-yl)hexyl]carbazole (**5**) and 1,6-di-[3-(1,3-dioxoindan-2-yl-methylene)carbazol-9-yl)hexane (**6**) were prepared by reactions of compounds (**3**) or (**4**) with excess of indan-1,3-dione in 1,4-dioxane or ethanol, respectively.

The newly synthesized derivatives were confirmed by mass spectrometry and ^{1}H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The derivatives were soluble in common organic solvents (THF, chloroform, DMF, chlorobenzene) at room temperature. Solubility of the materials of 10–15 milligrams in one millilitre of the solvent was suitable for preparation of transparent thin films by spin coating from solution method.

The behaviour under heating of the synthesized materials **5** and **6** was studied by DSC and TGA under a nitrogen atmosphere. It was observed during the TGA analysis that the objective materials have very high thermal stability, and their temperatures of 5% mass loss (T_d) are in the range of 398- 402°C. The thermal resistance of these derivatives almost do not depend on their chemical substitution. For example, compound **6** containing two 1,3-dioxoindan-2-ylmethylene groups has the highest T_d (402°C), however the value is rather close with that of mono-substituted derivative **5** ($T_d = 398$°C).

DSC experiment confirmed that both the derivatives were obtained as crystalline material by re-crystallisation from solutions; however they readily formed glasses with high glass transition temperatures (T_g) when their melt samples were cooled on standing in air or with liquid nitrogen. The DSC thermograms of **5** are shown in Figure 1 as an example. When the crystalline sample was heated, the endothermic peak due to melting was observed at 188°C. When the melt sample was cooled down and heated again, the glass-transition phenomenon was observed at 80°C and on further heating no peaks due to crystallisation and melting appeared. The crystalline sample of twin derivative **6** demonstrated the analogues behaviour.

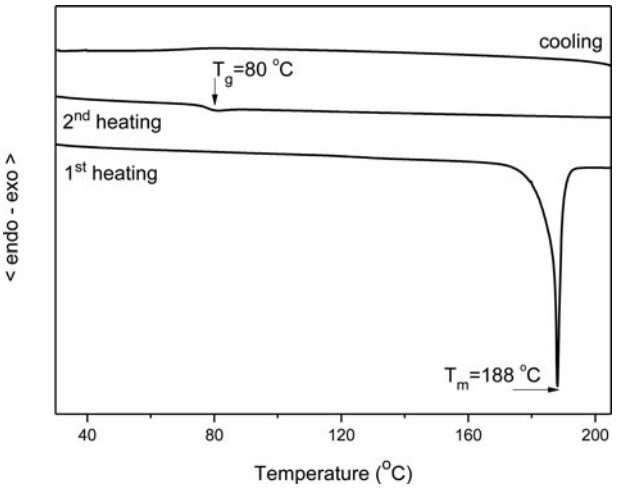


Figure 1. DSC curves of the material **5**.

It melted on first heating at 275°C and formed amorphous material with T_g of 114°C upon cooling. The results demonstrate that new host materials could form thin amorphous films suitable for OLED devices. It was also observed during the DSC analysis that the thermal transitions of the derivatives depended on their chemical structures. For example, the T_g value of di-substituted compound **6** was found to be considerably higher than that of derivative **5** having only one 1,3-dioxoindan-2-ylmethylene group in its structure.

To evaluate the performance of the new host materials **5** and **6**, blue phosphorescent OLEDs were fabricated using blue emitter iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N,C2′*]picolinate (**FIrpic**) as the guest. The structure of the multilayer devices was: ITO/PEDOT:PSS/host **5** or **6** doped with **FIrpic**/TPBi/LiF/Al. The fabrication is described in Experimental part. In all the formed devices containing hosts of **5** or **6**, the electrophosphorescence was found to originate only from the guest at different bias voltages. No host and doped transport molecular emission was visible from the OLED devices, indicating an efficient energy transfer or charge transfer from the hosts to the guest as well as the sufficient injection of both holes and electrons into the emitting layer.

Figure 2 shows characteristics of the formed devices. The OLED prepared using di-substituted twin derivative **6** (1,6-di-[3-(1,3-dioxoindan-2-yl-methylene)carbazol-9-yl)hexane) exhibited turn-on voltage of 5.2 V, maximum brightness of 115 cd/m^2 and photometric efficiency of 2.17 cd/A. The device prepared using mono-substituted derivative **5** (3-(1,3-dioxoindan-2-ylmethylene)-9-[6-(carbazol-9-yl)hexyl]carbazole) as the host exhibited better overall performance with low turn-on voltage of 5.0 V, maximum brightness of about 220 cd/m^2 and maximal photometric efficiency of about 2.7 cd/A. For the technically important brightness of 100 cd/m^2, the efficiency of the device containing host **5** was above 2.5 cd/A. It should be pointed out that these characteristics were obtained in non-optimized test devices under ordinary laboratory conditions. The device performance may be further improved by an optimization of the layer thicknesses and processing conditions.

In conclusion, new carbazole- indan-1,3-dione -based low molecular weight derivatives were synthesized and characterized by mass spectrometry and ^{1}H NMR spectroscopy. The amorphous derivatives show very high thermal stability (T_{ID}: 398- 401°C) and form thin amorphous films with high glass transition temperatures of 80–114°C. The synthesised materials were tested as hosts in blue phosphorescent OLEDs with iridium(III)[bis

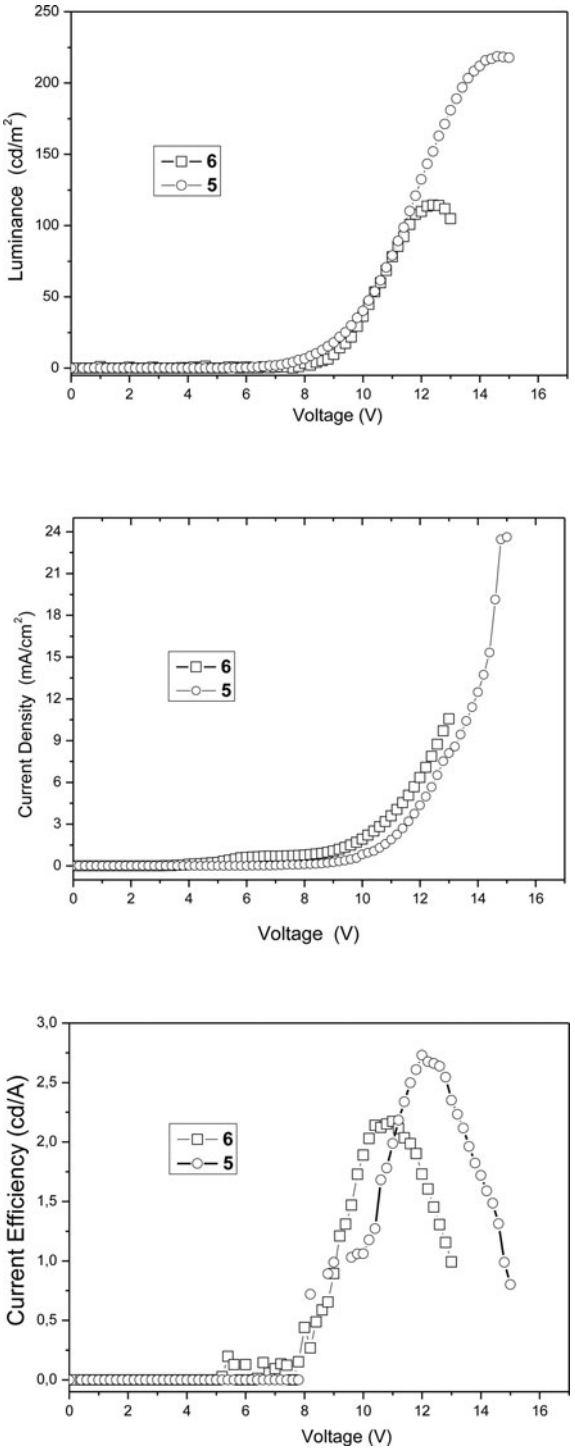


Figure 2. OLED characteristics of hosts **5** or **6**-based blue devices with **FIrpic** guest.

(4,6-difluorophenyl)-pyridinato-*N*,*C2′*]picolinate as the guest. The device with the host based on 3-(1,3-dioxoindan-2-ylmethylene)-9-[6-(carbazol-9-yl)hexyl]carbazole exhibited the best overall performance (turn-on voltage: 5.0 V; maximum photometric efficiency: 2.73 cd/A; maximum brightness: 220 cd/m^2).

Acknowledgments

Financial support of this research by the Research Council of Lithuania (project APP1/2016) is gratefully acknowledged.

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