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Fluorenes substituted with fluorophenyl, difluorophenyl or trifluorophenyl fragments as materials for organic light emitting diodes

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ABSTRACT

9,9-Diethylfluorenes substituted with two fluorophenyl, difluorophenyl or trifluorophenyl fragments were synthesized by the multi-step synthetic rout. The materials were characterized by ^{1}H NMR spectroscopy, mass spectrometry, differential scanning calorimetry and thermogravimetric analyses. Some of the electro-active derivatives could form thin amorphous films and were tested as solution processed hole transporting layers in organic light- emitting diodes with Alq_3 as the emitter and electron transporting material. Some of the electroluminescent devices demonstrated turn voltage of 5.5 V, a maximal photometric efficiency of about 1.0 cd/A and maximum brightness exceeding 960 cd/m^2.

KEYWORDS

Electro-active material; amorphous material; glass transition temperatures; electroluminescent device; photometric efficiency

1. Introduction

Organic light- emitting diodes (OLEDs) based on organic low molar mass materials or polymers have attracted much attention because of their potential use in flat panel displays and lighting applications [1–6]. It was demonstrated that efficient OLEDs can be obtained only by building multilayer structures [7–11]. One approach that has been employed to improve efficiency of the devices is the appliance of effective hole-transporting layers in the multilayer OLEDs [12–14].

Carbazole or triarylamine-containing polymers and low-molecular-weight derivatives are among the most studied hole transporting materials for optoelectronic and electronic applications due to high hole mobility in their layers and high thermal stability of the materials [15, 16]. We have described earlier several groups of carbazole, phenothiazine as well as indole based hole transporting materials [17–20]. Fluorene containing materials are widely known as derivatives for light emitting layers of OLED devices, however it was also demonstrated that fluorenyl fragments containing derivatives serve also as effective hole-transporting materials [21, 22]. Here we describe synthesis and properties of new fluorophenyl, difluorophenyl or trifluorophenyl substituted fluorenes, which were characterized as materials for hole transporting layers of OLED devices.

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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 thermos-system. Thermogravimetric analysis (TGA) was performed on a TGAQ50 apparatus. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10°C/min.

The multilayer electroluminescent devices were fabricated on glass substrates and had the typical structure with the organic layers sandwiched between a bottom ITO anode and a top metal (Al) cathode. The ITO-coated glass substrates were carefully cleaned and treated with UV/ozone right before deposition of the organic layers. The hole-transporting layers (HTL) were prepared by spin-coating from chloroform solutions (5mg/ml) of the derivatives **3** or **4**. Tris(quinolin-8-olato)aluminium (Alq_3) was used as green light emitter as well as electron transporting material. Evaporation of Alq_3 layer as well as of LiF /Al cathode was done at a pressure of 4×10^{-4} torr in vacuum evaporation equipment. The final structure of the devices was ITO/HTLs of **3** or **4** (40 nm)/Alq_3(80 nm)/LiF(1 nm)/Al(100 nm). Current-voltage and luminance-voltage characteristics of the OLEDs were recorded as we described earlier [23].

2.2. Materials

2,7-Dibromofluorene (**1**), 4-fluorophenyl boronic acid, 3,5-difluorophenyl boronic acid, 2,4,6-trifluorophenyl boronic acid, iodoethane, tetra-N-butylammonium chloride, bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), Alq_3, sodium hydroxide and potassium hydroxide were purchased from Aldrich and used as received.

2,7-Dibromo-9,9-diethylfluorene (**2**) was synthesized from 2,7-dibromfluorene by alkylation with an excess of iodoethane under basic conditions by similar procedure as it was described earlier [24].

2,7-Di(4-fluorophenyl)-9,9-diethylfluorene (**3**). 1g (2.6 mmol) of 2,7-dibromo-9,9-diethylfluorene (**2**), 0.9 g (7.2 mmol) of 4-fluorophenyl boronic acid, 0.07 g (0.1 mmol) of $PdCl_2(PPh_3)_2$ and 0.7 g (13.0 mmol) of powdered potassium hydroxide were stirred in 15 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 ethyl acetate. The combined extract was dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:10) as an eluent. Yield: 0.83 g of yellow crystals. M.p.: 109°C (DSC).

MS (APCI$^+$, 20 V): 411.1 ([M + H], 100%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.76 (dd, 2H, $J_1 = 0.6$Hz, $J_2 = 7.8$Hz, Ar), 7.66-7.59 (m, 4H, Ar), 7.56-7.49 (m, 4H, Ar), 7.21-7.11 (m, 4H, Ar) 2.10 (q, 4H, $J = 7.2$Hz, 2 × $\underline{CH_2}CH_3$), 0.40 (t, 6H, $J = 7.2$Hz, 2 × $CH_2\underline{CH_3}$).

2,7-Di(3,5-difluorophenyl)-9,9-diethylfluorene (**4**). 1g (2.6 mmol) of 2,7-dibromo-9,9-diethylfluorene (**2**), 1.1 g (6.5 mmol) of 3.5-difluorophenyl boronic acid, 0.07 g (0.09 mmol) of $PdCl_2(PPh_3)_2$ and 0.7 g (13.0 mmol) of powdered potassium hydroxide were stirred in 15 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 ethyl acetate. The combined extract was dried over anhydrous Na_2SO_4. The

crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:10) as an eluent. Yield: 0.95g of yellow crystalline material. M.p.: 218°C (DSC).

MS (APCI$^+$, 20 V): 447.1 ([M + H], 100%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.83 (d, 2H, $J = 8.1$Hz, Ar), 7.60-7.51 (m, 4H, Ar), 7.24-7.16 (m, 4H, Ar), 6.86-6.76 (m, 2H, Ar) 2.14 (q, 4H, $J = 7.2$Hz, 2 × $\underline{CH_2}CH_3$), 0.39 (t, 6H, $J = 7.2$Hz, 2 × $CH_2\underline{CH_3}$).

2,7-Di(2,4,6-trifluorophenyl)-9,9-diethylfluorene (**5**). 1g (2.6 mmol) of 2,7-dibromo-9,9-diethylfluorene (**2**), 1 g (5.7 mmol) of 2,4,6-trifluorophenyl boronic acid, 0.07 g (0.09 mmol) of $PdCl_2(PPh_3)_2$ and 0.7 g (13.0 mmol) of powdered potassium hydroxide were stirred in 15 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 ethyl acetate. The combined extract was dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:3) as an eluent. Yield: 0.9 g of brown crystals. M.p.: 152°C (DSC).

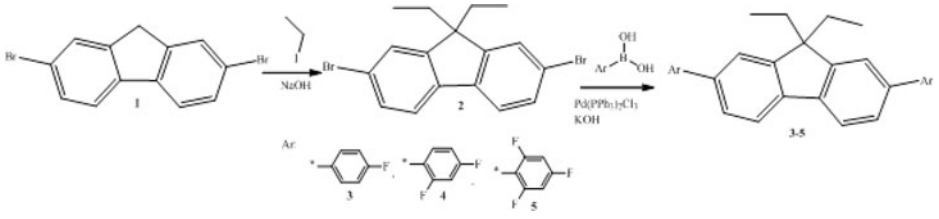
MS (APCI$^+$, 20 V): 483.1 ([M + H], 100%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.52–7.50 (m, 4H, Ar), 7.47-7.42 (m, 6H, Ar), 1.98 (q, 4H, $J = 7.5$Hz, 2 × $\underline{CH_2}CH_3$), 0.31 (tr, 6H, $J = 7.5$Hz, 2 × $CH_2\underline{CH_3}$).

3. Results and discussion

The synthesis of the electroactive materials, i.e., 2,7-diaryl-9,9-diethylfluorenes (3-5) containing two fluorophenyl, difluorophenyl or trifluorophenyl fragments was carried out by a multi-step synthetic route as shown in Scheme 1. Firstly, 2,7-dibromo-9,9-diethylfluorene (1) was synthesized by alkylation of commercially available 2,7-dibromofluorene with ethyl iodide. 2,7-Diaryl-9,9-diethylfluorenes (3-5) were then prepared by Suzuki reaction [25] of the 2,7-dibromo-9,9-diethylfluorene and an excess of 4-fluorophenyl boronic acid, 2,4-difluorophenyl boronic acid or 2,4,6-trifluorophenyl boronic acid, respectively.

The synthesized derivatives all were identified by mass spectrometry and ^{1}H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The materials all were soluble in common organic solvents and their thin films could be prepared by spin coating from solutions.

The behaviour under heating of the synthesized materials **3** – **5** was studied by DSC and TGA under a nitrogen atmosphere. It was observed during the TGA analysis that the objective materials have sufficient thermal stability, and their temperatures of 5% mass loss (T_{ID}) are in the range of 260–279°C. It was observed that the thermal resistance of these derivatives depends directly on their chemical substitution. The compound **3** containing two fluorophenyl fragments demonstrated the highest T_{ID} (279°C). Trifluorophenyl di-substituted derivative **5** contains the lowest T_{ID} of 260°C. The T_{ID} value of difluorophenyl-substituted compound **4** was 272°C.



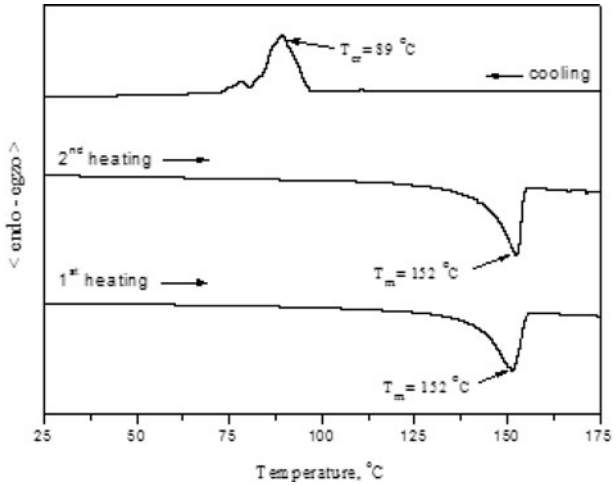


Figure 1. DSC curves of compound **5**. Heating rate: 10°C/min.

The thermal transitions under heating of the synthesized derivatives **3** – **5** was studied by DSC. All the compounds were obtained after synthesis as crystalline materials as confirmed by the experiment, however some of them could form also amorphous materials by fast cooling of their melts or by spin coating from solutions. The DSC thermo-grams of compound **5** are shown in Fig. 1 as an example. When the crystalline sample was heated during the experiment, the endothermic peak due to melting was observed at 152°C. When the melt sample was cooled down, its crystallization was observed at 89°C to form the same crystals, which were obtained by crystallization from solution. The compound **4** demonstrated an analogous behaviour during the DSC test. When its crystalline sample was heated during the experiment, melting was observed at 218°C. When the melt sample was cooled down, it formed again the crystalline material with crystallization temperature at 182°C. It was observed during the analysis that the thermal transitions of the derivatives **4** and **5** depend on their chemical structure. For example, the values of melting temperature (T_m) and of crystallization temperature (T_{cr}) for difluorophenyl-substituted compound **4** was found to be considerably higher than those of derivative **5** having trifluorophenyl substituents in its structure.

Compounds **3** demonstrated different behaviour during the DSC experiments. The crystalline sample of **3** melted at 109°C on first heating and formed glass with glass transition temperature of 51°C upon cooling. When the amorphous sample was heated again, an exothermic peak due to crystallisation was observed at 82°C to give the same crystals, which were obtained after synthesis and melted at 109°C. It could be observed that tendency for crystallization of the synthesized materials depends on number of fluorine atoms in the molecules. The derivatives **4** and **5** having four or six fluorine atoms demonstrate strong tendency for crystallization due to close and suitable packing of the molecules into crystals. The material **3** having only two fluorine atoms can form amorphous material. This observation demonstrates that the derivative could form thin and homogenous amorphous layers and is the most suitable for preparation of charge transporting layers for OLED devices.

The compounds **3** and **4**, which formed homogenous thin films by spin coating from solutions, were tested in OLEDs as materials for hole transporting (HT) layers. The material **5** demonstrated strong tendency for crystallization and could not form homogenous films which could be suitable for application in OLED devices. The two layer OLED devices were

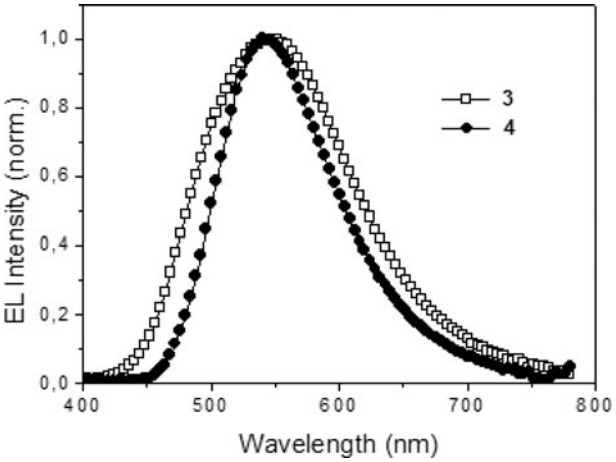


Figure 2. EL spectra of the devices: ITO/**3** or **4**/Alq_3/LiF/Al.

prepared using **3** or **4** as HT layers and Alq_3 as the electroluminescent (EL) and electron transporting material. Details of fabrication of the devices are described in Experimental part.

When positive voltage was applied for the OLEDs, the bright green electroluminescence of Alq_3 was observed from both the devices with an emission maximum at around 520 nm as it is shown in Fig. 2. This implies that the positive charge mobility in the HT layers of **3**

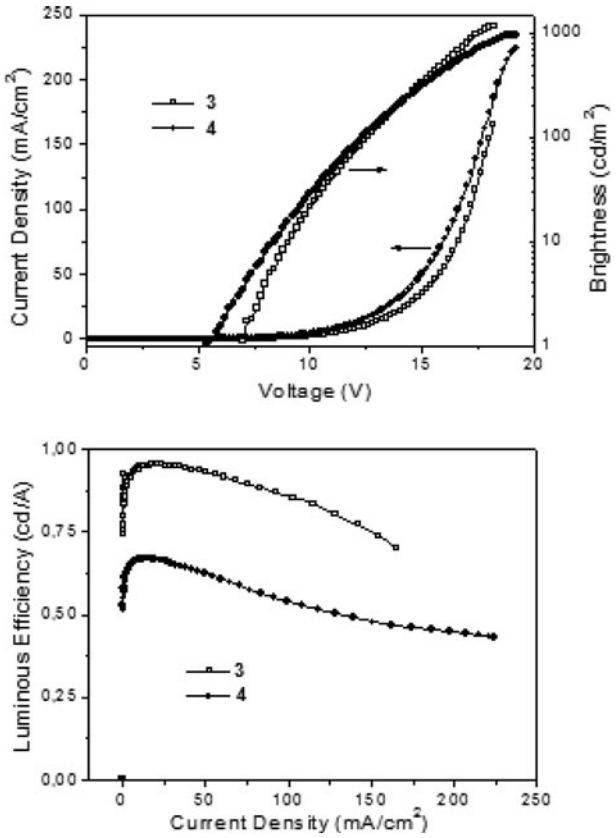


Figure 3. OLED characteristics of the devices with the configuration: ITO/**3** or **4**/Alq_3/LiF/Al.

and **4** was fully sufficient for an effective charge carrier recombination occurring within the Alq_3 layer. An exciplex formation at the interface between the hole transporting layers of **3** or **4** and Alq_3 emitter layer was not observed.

Figure 3 shows current density-voltage-brightness and efficiency – current density (c) characteristics for the OLEDs containing the HT layers of **3** or **4**. The devices with the synthesized hole transporting materials exhibit turn-on voltages of 5.4–7.0 V (defined as the voltage where electroluminescence becomes detectable) and a maximum brightness of 960–1160 cd/m^2. Maximal current efficiencies of the OLEDs are 0.96 cd/A and 0.67 cd/A for the materials **3**- and **9**-based devices, correspondingly, and are stable in the observed current density window up to 160 mA/cm^2 and 220 mA/cm^2. It should be pointed out that these device properties were obtained in non-optimized solution processed devices under ordinary laboratory conditions. The device performance may be further improved by an optimization of the layer thicknesses and processing conditions [26].

In conclusion, 9,9-diethylfluorenes substituted with two fluorophenyl, difluorophenyl or trifluorophenyl fragments have been synthesized and characterized as charge transporting materials for electroluminescent devices. Some of the compounds form solution processed homogeneous electro-active layers. The derivatives have been tested as hole transporting materials in bilayer organic light emitting diodes with Alq_3 as the emitter and electron transporting layer. A device with hole transporting layers of 2,7-di(4-fluorophenyl)-9,9-diethylfluorene exhibited good overall performance with turn on voltage of 5.4 V, maximum brightness of about 960 cd/m^2 and photometric efficiency of about 1 cd/A.

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