



3-Aryl substituted 9-alkylcarbazoles as tailored building blocks for hole transporting materials of OLEDs

G. Krucaite^a, R. Griniene^a, D. Mazetyte^a, G. Puckyte^a, J.V. Grazulevicius^a, Y.C. Hsieh^b, Y.L. Chen^b, J.H. Jou^{b,*}, S. Grigalevicius^{a,*}

^a Department of Organic Technology, Kaunas University of Technology, Radvilenu plentas 19, LT50254 Kaunas, Lithuania

^b Department of Materials Science and Engineering, National Tsing-Hua University, No. 101, Kaungfu Rd., Hsin-Chu 30013, Taiwan, ROC

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ABSTRACT

4-Fluorophenyl, phenyl or naphthyl substituted 9-alkylcarbazoles were synthesized by the multi-step synthetic route. The materials were characterized by elemental analyses, mass and ¹H NMR spectroscopy as well as by electron photoemission technique. These derivatives were tested for hole injecting and transporting layers in OLEDs with Alq₃ as the emitter. The 3-(1-naphthyl)-9-ethylcarbazole-based OLED exhibited the best performance with a turn-on voltage of ~3 V, a maximal current efficiency of 0.85 cd/A and maximum brightness of 1270 cd/m². The device was modified with PEDOT:PSS hole injection layer and demonstrated lower turn-on voltage of ca. 3.0 V, combined with a maximum brightness of 9524 cd/m² and a maximum photometric efficiency of ca. 5 cd/A.

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1. Introduction

Organic light-emitting diodes (OLEDs) based on organic small molecules and polymers have attracted much attention because of their potential use in flat panel displays and lighting [1–4]. Efficient OLEDs can be obtained only by building multilayer structures. For example, the appliance of effective hole transporting layers in the multilayer OLEDs could reasonably improve characteristics of the devices [5,6]. Small modifications of building blocks of the hole transporting derivatives can dramatically change their electronic properties as well as charge transport. Therefore, knowledge of reliable structure–property relations is essential for a rational design of the charge transporting materials.

Carbazole-containing polymers and low-molecular-weight derivatives are among the most studied materials for multilayer electronic devices due to their high hole mobility [7,8]. We have synthesized earlier series of hole-transporting carbazole-, [3,3]bicarbazole- and indolo[3,2-b]carbazole-based derivatives [9–12]. It was observed that aryl substituted indolo[3,2-b]carbazole derivatives demonstrate better charge transporting properties than the derivatives containing un-substituted hetero-aromatic rings [13]. In this work, we have synthesized and studied 3-aryl

substituted 9-alkylcarbazoles as tailored building blocks for hole transporting materials.

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. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The ionization potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [14]. The measurement method was, in principle, similar to that described by Miyamoto et al. [15]. The samples for the ionization potential measurements were prepared as follows [16]. The materials were dissolved in THF and were coated on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of this layer is not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, the MKM layer is conductive enough to avoid charge accumulation on it during the measurements. The thickness of the layers was 0.5–1 μm.

* Corresponding authors.

E-mail addresses: jjou@mx.nthu.edu.tw (J.H. Jou), saulius.grigalevicius@ktu.lt (S. Grigalevicius).

The multilayer OLEDs were fabricated on glass substrates and had the typical structure with the organic layers sandwiched between a bottom ITO (125 nm) anode and a top metal cathode: ITO/**6**, **7** or **8**/Alq₃/(LiF/Al). Before use in device fabrication, 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 a 45 nm layer of the derivatives **6**, **7** or **8** from their solutions. Tris(quinolin-8-olato)aluminum (Alq₃) was used as green light emitter. Evaporation of Alq₃ as well as of LiF/Al cathode was done at a pressure of 10⁻⁵ Torr in vacuum evaporation equipment. Material **8**-based device, containing an additional PEDOT:PSS hole injecting layer, was also studied. The PEDOT:PSS layer (35 nm) was deposited by spin-coating and was then heated at 120 °C for 30 min. It was described earlier that these conditions are suitable for the preparation of PEDOT:PSS layers with optimum electrical properties [17]. The current–voltage and luminance–voltage characteristics of the devices were recorded as we described earlier [18].

2.2. Materials

9H-carbazole (**1**), 2-ethylhexylbromide, 9-ethylcarbazole (**4**), 1-naphthalene boronic acid, phenyl boronic acid, 4-fluorophenyl boronic acid, bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂), Alq₃, and potassium hydroxide were purchased from Aldrich and used as received.

3-Iodo-9H-carbazole (**2**), 3-iodo-9-ethylcarbazole (**5**) [19] and 3-iodo-9-(2-ethylhexyl)carbazole (**3**) [20] were synthesized according to the procedures outlined in literature.

3-(4-Fluorophenyl)-9-(2-ethylhexyl)carbazole (**6**): 2.0 g (4.93 mmol) of 3-iodo-9-(2-ethylhexyl)carbazole (**3**), 1.4 g (10 mmol) of 4-fluorophenyl boronic acid, 0.14 g (0.2 mmol) of PdCl₂(PPh₃)₂ and 1.38 g (24.6 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 chloroform. The combined extract was dried over anhydrous Na₂SO₄. The crude product was purified by silica gel column chromatography using the mixture of ether and hexane (vol. ratio 1:50) as an eluent. Yield: 0.57 g (31%) of white crystals. M.p.: 62 °C (DSC).

MS (APCI⁺, 20 V): 378.6 ([M+1], 100%). ¹H NMR spectrum (CDCl₃, δ, ppm): 8.23 (s, 1H, Ar), 8.12 (d, 1H, J = 7.8 Hz, Ar), 7.71–7.12 (m, 9H, Ar), 4.14 (d, 2H, NCH₂, J = 7.5 Hz), 2.14–2.01 (m, 1H, CH(CH₂)₃), 1.51–1.24 (m, 8H, 4 × CH₂), 1.01–0.81 (m, 6H, 2 × CH₃). Elemental analysis for C₂₆H₂₈FN % Calc.: C 83.61, H 7.56, N 3.75; % Found: C 83.59, H 7.52, N 3.71.

3-Phenyl-9-ethylcarbazole (**7**): 1.5 g (5.5 mmol) of 3-iodo-9-ethylcarbazole (**5**), 1.2 g (10 mmol) of phenyl boronic acid, 0.09 g (0.1 mmol) of PdCl₂(PPh₃)₂ and 0.94 g (16.7 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 chloroform. The combined extract was dried over anhydrous Na₂SO₄. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:50) as an eluent. Yield: 0.61 g (48%) of white crystals. M.p.: 124 °C (DSC).

MS (APCI⁺, 20 V): 272.5 ([M+1], 100%). ¹H NMR spectrum (CDCl₃, δ, ppm): 8.31 (s, 1H, Ar), 8.14 (d, 1H, Ar, J = 7.8 Hz), 7.74–7.71 (m, 3H, Ar), 4.38 (q, 2H, NCH₂, J = 7.2 Hz), 1.45 (t, 3H, CH₃, J = 7.2 Hz). Elemental analysis for C₂₀H₁₇N % Calc.: C 88.52, H 6.31, N 5.16; % Found: C 88.49, H 6.36, N 5.12.

3-(1-Naphthyl)-9-ethylcarbazole (**8**): 1.5 g (5.5 mmol) of 3-iodo-9-ethylcarbazole (**5**), 1.73 g (10 mmol) of 1-naphthalene boronic acid, 0.09 g (0.13 mmol) of PdCl₂(PPh₃)₂ and 0.94 g

(16.8 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 chloroform. The combined extract was dried over anhydrous Na₂SO₄. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:30) as an eluent. Yield: 0.43 g (29%) of white crystals. M.p.: 107 °C (DSC).

MS (APCI⁺, 20 V): 322.5 ([M+1], 100%). ¹H NMR spectrum (CDCl₃, δ, ppm): 8.27 (s, 1H, Ar), 8.18–8.01 (m, 4H, Ar), 8.01–7.68 (m, 9H, Ar), 4.49 (q, 2H, NCH₂, J = 7.2 Hz), 1.56 (t, 3H, CH₃, J = 7.2 Hz). Elemental analysis for C₂₄H₁₉N % Calc.: C 89.68, H 5.96, N 4.36; % Found: C 89.71, H 5.98, N 4.33.

3. Results and discussion

The synthesis of 3-aryl substituted 9-alkylcarbazoles (**6–8**) was carried out by a multi-step synthetic route as shown in Scheme 1. 3-Iodo-9H-carbazole (**2**) was synthesized from commercially available 9H-carbazole (**1**) by Tucker iodination procedure [19]. The iodo derivative **2** was converted to 3-iodo-9-(2-ethylhexyl)carbazole (**3**) by alkylation with an excess of 2-ethylhexylbromide under basic conditions. The final material, 3-(4-fluorophenyl)-9-(2-ethylhexyl)carbazole (**6**) was prepared by Suzuki reaction of the compound **3** with an excess of 4-fluorophenyl boronic acid. It is known that fluorine is an electron withdrawing atom. So, the 4-fluorophenyl based carbazole compound (**6**) was chosen as OLED material containing higher ionization potential than that of phenyl-substituted derivatives **7**.

9-Ethylcarbazole based materials **7** and **8** were prepared from commercially available 9-ethylcarbazole (**4**). Compound **4** was converted to 3-iodo-9-ethylcarbazole (**5**) using Tucker iodination method [19]. Phenyl- and naphthyl-substituted derivatives **7** and **8** were prepared by Suzuki reaction of the compound **5** with an excess of phenyl boronic acid or 1-naphthalene boronic acid, correspondingly.

The synthesized derivatives **6–8** were identified by elemental analyses, mass spectrometry and ¹H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The materials are soluble in common organic solvents. Transparent thin films of these materials could be prepared by spin coating from solutions or by vacuum evaporation.

The ionization potentials (*I*_p) of layers of the compounds synthesized were measured by the electron photoemission method. The photoemission spectra of thin films of the compounds **6–8** as well as values of *I*_p are presented in Fig. 1. The *I*_ps are very close to 5.8 eV for all the compounds. However, it could be observed that the values of *I*_p of the newly synthesized compounds are lower than that of widely used carbazoyl-containing polymer-poly(9-vinylcarbazole) (PVK, *I*_p > 5.9 eV) [21] as well as of other derivatives having un-substituted carbazole rings [22]. The data demonstrate that thin layers of the materials **6–8** could be suitable for application in optoelectronic devices as positive charges transporting materials. Their layers should demonstrate better hole injecting and transporting properties in multilayer devices than that of widely used PVK [21].

All the synthesized materials **6–8** were tested in OLEDs of the form ITO/**6**, **7** or **8**/Alq₃/(LiF/Al) as hole transporting materials. The multilayer OLED devices were prepared using Alq₃ for the electroluminescent (EL)/electron transporting layers. The cathode used was aluminum with a thin LiF electron injection layer. When a positive voltage was applied the bright green electroluminescence of Alq₃ was observed with an emission maximum at around 520 nm. No spectroscopic sign for exciplex formation at the

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