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[3,3′]Bicarbazolyl-based enamines as hole-transporting materials

R. PASPIRGELYTE[a], V. VAITKEVICIENE[a,d], S. GRIGALEVICIUS[a], J.V. GRAZULEVICIUS[a*],
V. JANKAUSKAS[b], V. LINONIS[c]
[a]*Department of Organic Technology, Kaunas University of Technology,*
Radvilenu plentas 19, LT50254, Kaunas, Lithuania
[b]*Department of Solid State Electronics, Vilnius University, Sauletekio aleja 9, LT10222, Vilnius, Lithuania*
[c]*Physical Education and Sports Center, Kaunas University of Technology, A. Pureno 18, Kaunas, Lithuania*
[d]*Lithuanian Energy Institute, 3 Breslaujos str., LT-44403, Kaunas, Lithuania*

[3,3′]Bicarbazolyl - based enamines have been synthesized by the multi-step synthetic rout. Full characterization of their structure by nuclear magnetic resonance and mass spectrometry as well as by infrared spectroscopy is presented. The synthesized materials were examined by various techniques including differential scanning calorimetry, ultraviolet and photoluminescent spectrometry, electron photoemission spectrometry and time of flight techniques. Electron photoemission spectra of the amorphous layers of the synthesized enamines revealed the ionization potentials of ca. 5.5 eV. Time-of-flight hole drift mobilities in the layers of bisphenol Z polycarbonate molecularly doped with 33 - 50 wt. % of [3,3′]-bicarbazolyl - based enamines ranged from 10^{-5} to 10^{-4} cm^2/Vs at high electric fields.

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1. Introduction

Organic semiconductors are used for the fabrication of different electronic and optoelectronic devices such as light emitting diodes, photovoltaic cells, organic thin film transistors, electrophotographic photoreceptor [1-4]. Among organic semiconductors hole-transporting materials are so far much wider synthesized, studied and applied. For various field of application hole-transporting materials with the certain complex of properties are required. No reliable theories for the design of organic semiconductors having an optimal combination of the required properties have yet been developed. Consequently, such materials need to be discovered experimentally. Different electrophores are used in the design and synthesis of organic hole-transporting compounds. [3,3′]Bicarbazolyl unit is interesting for this purpose for the following reasons: 9H-carbazole is a cheap starting material; [3,3′]bicarbazolyl is a fully aromatic unit providing a high thermal, morphological, chemical and environmental stability; its nitrogen atoms can be easily substituted with a wide variety of functional groups; the layers of the [3,3′]bicarbazolyl-based derivatives have lower ionization potentials than those of carbazole-based materials [5,6]. On the other hand aromatic enamines are materials which demonstrate promising optoelectronic properties, however their synthesis and properties are little studied [7].

In this presentation we report on the synthesis of [3,3’]bicarbazolyl-based enamines. Designing these relatively large molecules we aimed to render them good glass-forming ability. Enlarged systems of conjugated π electron systems were expected to ensure good charge transport properties.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using Varrian Unity Inova (300 MHz) apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FTIR spectra were recorded using Perkin Elmer FT-IR System. UV spectra were measured with Spectronic Unicam Genesys 8 spectrometer. Fluorescence (FL) spectra were recorded with Hitachi MPF- 4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer Pyris Diamond calorimeter. The DSC experiments were performed in a nitrogen atmosphere at a heating rate of 10 ^{o}C/min.

Ionization potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [8,9].

Hole drift mobilities in the layers of the synthesized compounds molecularly dispersed in a polymer host bisphenol Z polycarbonate (PC-Z) were measured by xerographic the time of flight technique [10,11]. The samples for the charge carrier mobility measurements were prepared as we described earlier [12]. The thickness of the charge transport layers varied in the range of 8-10 μm.

2.2. Materials

9H-Carbazole (**1**), 1-bromohexane, 2-ethylhexylbromide, 2,2-diphenylacetaldehyde, 2-phenylpropionaldehyde, iron(III) chloride, tetra-n-butylammonium hydrogen sulfate (TBAS) and (±)-camphor-10-sulfonic acid were purchased from Aldrich and used as received.

9H,9'H-[3,3']Bicarbazolyl (**2**) was obtained by chemical oxidation of 9H-carbazole (**1**) in the presence of $FeCl_3$ as we described earlier [13].

MS ($APCI^+$, 20 V): 334 ([M+1], 95 %).

^1H NMR spectrum (DMSO, δ, ppm): 11.31 (s, 2H, NH), 8.55 (s, 2H), 8.27 (d, 2H, J=7.8 Hz), 7.84 (d, 2H, J=9 Hz), 7.62 (d, 2H, J=8.4 Hz), 7.55 (d, 2H, J=7.8 Hz), 7.46-7.4 (t, 2H, J=7.0 Hz), 7.25-7.18 (t, 2H, J=6.9 Hz).

IR (KBr): 3419 (N-H, Ar), 3048 (C-H, Ar), 1604, 1491, 1468, 1456, 1241, 753 (C=C, Ar).

9-(2-Ethylhexyl)-9'H-[3,3']bicarbazolyl (**3**). 2-Ethylhexyl bromide (3.86 g, 20 mmol) and TBAS (0.14 g, 0.4 mmol) were added to a stirred solution of 9H,9'H-[3,3']bicarbazolyl (**2**) (6.64 g, 14 mmol in 150 ml of THF). The mixture was heated to reflux, and powdered potassium hydroxide (1.12 g, 20 mmol) was added stepwise. When the reaction was over (TLC control) the inorganic salts were filtered off and the product was purified by silica gel column chromatography using hexane/ ethyl acetate (vol. ratio 8:1) as an eluent. The yield of compound **3** was 2.8 g.

MS ($APCI^+$, 20 V): 445 ([M+1], 98 %).

^1H NMR spectrum ($CDCl_3$, δ, ppm): 8.45 (d, 2H, J=4.5 Hz), 8.27-8.21 (m, 2H), 7.93 (bs, 1H, NH), 7.89-7.82 (m, 2H), 7.48-7.16 (m, 8H), 4.25 (d, J=7.2 Hz, NCH_2), 2.05-1.98 (m, 1H), 1.42-1.18 (m, 8H), 0.94-0.88 (m, 6H).

IR (KBr): 3405 (NH), 3049 (C-H, Ar), 2950, 2927, 2858 (C-H); 600 (C=C, Ar), 1490, 1459, (C=C, Ar), 1243, 749.

9-Hexyl-9'H-[3,3']bicarbazolyl (**4**). 1-Bromohexane (2.4 g, 15 mmol) and TBAS (0.14 g, 0.4 mmol) were added to a stirred solution of 9H,9'H-[3,3']bicarbazolyl (**2**) (6.9 g, 20 mmol in 100 ml of THF). The mixture was heated to reflux, and powdered potassium hydroxide (1.7 g, 30 mmol) was added stepwise. When the reaction was over (TLC control) the inorganic salts were filtered off and the product was purified by silica gel column chromatography using hexane/ ethyl acetate (vol. ratio 9:1) as an eluent. The yield of compound **4** was 1.6 g.

MS ($APCI^+$, 20 V): 417 ([M+1], 60 %).

^1H NMR spectrum (DMSO, δ, ppm): 11,29 (s, H, -NH), 7,16- 8,15 (m, 14H, -CH, Ar), 4,43-4,38 (m, 2H, NCH_2), 1,17-1,38 (m, 8H, $-CH_2CH_2CH_2CH_2-$), 0,87-0,90 (m, 3H, CH_3).

IR (KBr): 3419 (NH), 3049 (CH, Ar), 2923, 2853 (C-H), 1625, 1600, 1492, 1450 (C=C, Ar).

9-(2-Ethylhexyl)-9'-(2,2-diphenylvinyl)-[3,3']bicarbazolyl (**5**). 9-(2-Ethylhexyl)-9'H-[3,3']bicarbazolyl (**3**) (1.75 g, 4 mmol) was dissolved in the mixture of toluene (15 ml) and THF (10 ml) at 60 ºC. 2,2-Diphenylacetaldehyde (1.14 ml, 6 mmol) was added dropwise to the stirred reaction mixture and a catalytic amount of (±)-camphor-10-sulfonic acid was added. The solution was stirred at 60 ºC for 24 h. When the reaction was finished (TLC control), the solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography using using hexane/ diethyl ether (vol. ratio 15:1) as an eluent. The yield of compound **5** was 0.5 g.

MS ($APCI^+$, 20 V): 623 ([M+1], 100 %).

^1H NMR spectrum ($CDCl_3$, δ, ppm): 8.36 (s, 1H, Ar); 8.33 (s, 1H, Ar); 8.16 (d, 1H, J = 6.6 Hz, Ar); 8.1 (d, 1H, J = 6.6 Hz, Ar); 7.77 (d, 1H, J = 8.7 Hz, Ar); 7.64 (d, 1H, J = 8.5 Hz, Ar); 7.52 -7.36 (m, 8H, Ar); 7.35 -7.20 (m, 6H, Ar); 7.16 – 7.04 (m, 5H, Ar); 4.18 (d, 2H, J = 7.2 Hz, $N\underline{CH_2}$); 2.16 – 2.04 (m, 1H, $NCH_2\underline{CH}$); 1.44 – 1.24 (m, 8H, $NCH_2CH(\underline{CH_2}CH_3)\underline{CH_2CH_2CH_2}CH_3$); 0.96 – 0.84 (m, 6H, $NCH_2CH(CH_2\underline{CH_3})((CH_2)_3\underline{CH_3})$).

IR (KBr): 3051, 3024 (C-H, Ar); 2956, 2925, 2855 (C-H); 1616, 1599, 1573 (C=C, Ar); 1486, 1467, 1453 (C=C); 1220, 799, 767, 744, 697.

9-Hexyl-9'-(2-phenyl-2-methylvinyl)-[3,3']bicarbazolyl (**6**). 9-Hexyl-9'H-[3,3']bicarbazolyl (**4**) (1.4 g (3 mmol) was dissolved in the mixture of toluene (10 ml) and THF (15 ml) at 80 ºC. 2-Phenylpropionaldehyde (0.62 g, 5 mmol) was added dropwise to the stirred reaction mixture and a catalytic amount of (±)-camphor-10-sulfonic acid was added. The solution was stirred at 80 ºC for 24 h. When the reaction was finished (TLC control), the solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography using using hexane/ diethyl ether (vol. ratio 15:1) as an eluent. The yield of compound **5** was 0.14 g.

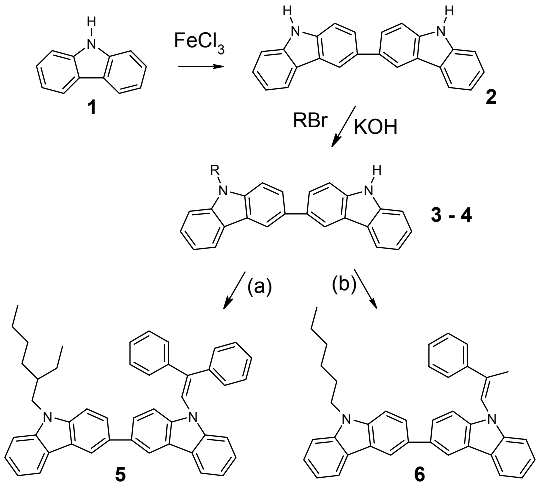
MS ($APCI^+$, 20 V): 533 ([M+1], 100 %).

^1H NMR spectrum ($CDCl_3$, δ, ppm): 8.43 (s, 2H, Ar); 8.26 – 8.17 (m, 2H, Ar); 7.95 (d, 2H, J = 8.4 Hz, Ar); 7.67 (d, 2H, J = 6.6 Hz, Ar); 7,6 – 7,12 (m, 12H, Ar); 4.33 (t, 2H, J = 7.3 Hz, $N\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$); 2.11 (s, 3H, $NCHC(C_6H_5)\underline{CH_3}$); 1.98 – 1.84 (m, 2H, $NCH_2\underline{CH_2}$); 1.48 – 1.24 (m, 6H, $NCH_2CH_2\underline{CH_2CH_2CH_2}CH_3$); 0.86 (t, 3H, J = 7.1 Hz, $N(CH_2)_5\underline{CH_3}$).

IR (KBr): 3047 (C-H, Ar); 2954, 2923, 2851 (C-H); 1624, 1599 (C=C, Ar); 1486, 1468, 1453 (C=C, Ar); 1231, 800, 744.

3. Results and discussion

[3,3']Bicarbazolyl based enamines (**5**, **6**) were prepared by three step synthetic route as shown in Fig. 1. The key starting compound 9H,9′H-[3,3′]bicarbazolyl (**2**) was obtained by chemical oxidation of 9H-carbazole (**1**) in the presence of $FeCl_3$ by a similar procedure as we described earlier [13]. The derivative **2** containing two secondary amino functions was mono-alkylated by 2-ethylhexyl bromide or 1-bromohexane, respectively, to provide the compounds with one secondary amino function (**3** and **4**). The aromatic enamines **5** and **6** were synthesized from the 9-alkyl-9'H-[3,3']bicarbazolyls and a corresponding aldehyde - 2,2-diphenylacetaldehyde or 2-phenylpropionaldehyde, respectively, using catalytic amount of (±)-camphor-10-sulfonic acid.



***Scheme 1**. a) 2,2-diphenylacetaldehyde and (±)-camphor-10-sulfonic acid; b) 2-phenylpropionaldehyde and (±)-camphor-10-sulfonic acid.*

The newly synthesized compounds were identified by mass-, IR- and ^{1}H NMR spectrometries. The data were found to be in good agreement with the proposed structures. Both the [3,3′]bicarbazolyl-based enamines (**5** and **6**) were obtained as amorphous materials after purification by column chromatography. The compounds are soluble in common organic solvents at the room temperature and form thin and transparent amorphous films by casting or spin-coating from their solutions.

The behaviour under heating of the compounds synthesized was studied by DSC. When the samples of the compounds were heated the glass-transitions were observed at 56 °C for **5** and at 52 °C for **6**, and no peaks due to crystallisation and melting appeared. Cooling down and the following repeated heating revealed only the glass transitions again. As an example, the DSC thermograms of **5** are shown in Fig. 1.

It is of interest to compare the glass transition temperatures (T_g) of the [3,3’]bicarbazolyl-based enamines with that of earlier reported 9,9’-dialkyl-[3,3’]bicarbazolyl derivatives [14]. The compounds containing two ethyl or butyl subtituents could be crystallized; however they formed amorphous films by casting from solutions. [3,3’]Bicarbazolyl derivatives having longer alkyl chains were viscous materials, i.e. their T_g are close to room temperature. It is evident that the replacement of one alkyl group by arylvinyl fragment increases T_g of the materials. The values of T_g of the enamines synthesyzed can be modified by attachment of the different alkyl chains to the [3,3’]bicarbazolyl core.

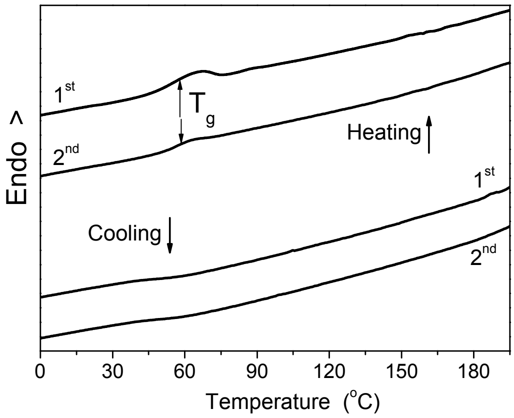


Fig. 1. DSC curves of compound 5.

UV absorption and FL spectra of dilute THF solutions of compounds **5** and **6** were recorded. The electronic absorption energies of the derivatives **5** and **6** are comparable. They absorb UV light in the region 230-370 nm and the λ_{max} values are at 245 and 310 nm. FL spectra of the dilute solutions of the compounds **5** and **6** have λ_{max} at ~ 405 nm. The spectrum of **5** is presented in Figure 2. For the comparison FL spectrum of 9,9’-diethyl-[3,3’]bicarbazolyl (BCz) is given in the Figure. It is evident that the λ_{max} of the fluorescence bands of the newly synthesized compounds are very close to that of BCz. This observation shows that the new molecules have similar conjugation length to that of 9,9’-dialkyl-[3,3’]bicarbazolyls. In the same manner ionization potentials (I_p) of amorphous layers of the compounds **5** and **6** are expected to demonstrate the similar values to those of 9,9’-dialkyl-[3,3’]bicarbazolyl derivatives.

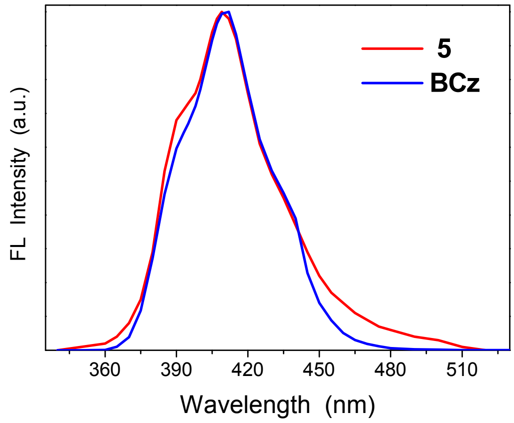


Fig. 2. FL emission spectra of dilute THF solutions (10^{-4} mol/l) of the derivative 5 and of BCz. Excitation wavelength 300 nm.

Electron photoemission spectra of the amorphous films of compounds **5** and **6** are presented in Fig. 3. The values of I_p are 5.53 eV for the film of **5** and 5.55 eV for the film of **6**. The I_p values of the materials synthesized are close to the I_p values of 9,9’-dialkyl-[3,3’]bicarbazolyl derivatives (I_p = 5.45 – 5.55 eV) [14].

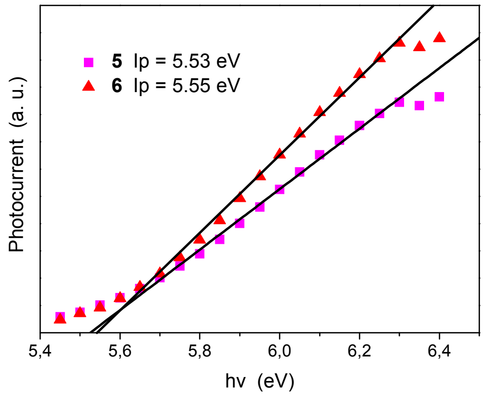


Fig. 3. Electron photoemission spectra of compounds 5 and 6.

The materials synthesized can be applied as components of electrophotographic photoreceptors. Holes would be easily injected into the layers of **5** and **6** from charge generation layers with I_p close to 5.5 eV. The I_p values for charge generation materials, i.e. widely used in electro-photographic photoreceptors pigments, such as titanyl phthalocyanines [15,16], perylene pigments [17] and bisazo pigments [17] are in the range of 5.2-5.6 eV. The I_p values of compounds **5** and **6** are rather close to that of indium-tin oxide (ITO), which is widely used as an anode in electroluminescent devices [19].

Time of flight measurements were used to characterize hole transport properties of compounds **5** and **6.** Charge mobilities were measured in the layers of the synthesized compounds molecularly dispersed in a polymer host PC-Z.

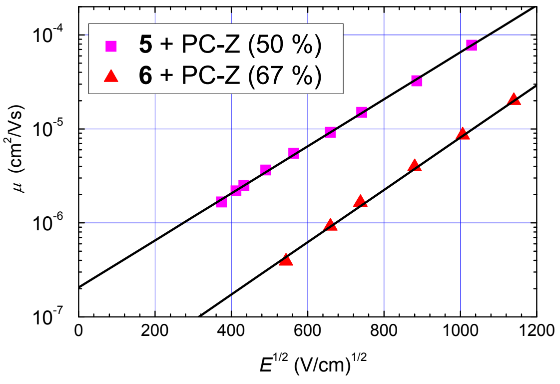


Fig. 4. Electric field dependencies of hole drift mobility in charge transport layers of compounds 5-6 molecularly doped in PC-Z.

The room temperature hole mobility (μ_h) showed a linear dependence on the square root of electric field (Figure 4). Such dependence is observed for the majority of non-crystalline organic systems and is attributed to the effects of disorder on the charge transport [**Error! Bookmark not defined.**]. The molecular dispersions of **5** with 50 wt.% in PC-Z demonstrated the μ_h values reaching 7×10^{-5} cm^2/Vs at an electric field of 10^6 V/cm at room temperature. It could be mentioned that μ_h in the layers of 9,9’-diethyl-[3,3’]bicarbazolyl dispersted in PC-Z (50 wt.%) reached only 3×10^{-6} cm^2/Vs at similar experimental conditions [14]. The layers of the molecular dispersion of **6** (33 wt.%) in PC-Z demonstrated the μ_h values reaching 10^{-5} cm^2/Vs at an electric field of 10^6 V/cm at room temperature. It should be mentioned that charge mobilities were estimated in the layers having only 33 - 50 wt.% of the electroactive materials **5** or **6**. The charge mobilities higher by ca. two orders of magnitude can be predicted for the amorphous films of the pure compounds.

In conclusion, we have synthesized [3,3’]bicarbazolyl based enamines, which form glasses with glass transition temperatures of ca. 50 °C. The values of ionization potentials of the amorphous layers of the synthesized compounds are ca. 5.5 eV. Time-of-flight hole drift mobilities in the layers of bisphenol Z polycarbonate molecularly doped with 33 - 50 wt. % of [3,3′]-bicarbazolyl - based enamines ranged from 10^{-5} to 10^{-4} cm^2/Vs at high electric fields.

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*Corresponding author: juozas.grazulevicius@ktu.lt