

# Vinyloxyethyl-substituted carbazole-based hydrazone and its adducts with diol and dithiol as glass-forming hole transport materials

Ruta Budreckiene<sup>a,1</sup>, Gintaras Buika<sup>a</sup>, Juozas Vidas Grazulevicius<sup>a,\*</sup>,  
Vygintas Jankauskas<sup>b</sup>, Birute Staniskiene<sup>c</sup>

<sup>a</sup> Department of Organic Technology, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania

<sup>b</sup> Department of Solid State Electronics, Vilnius University, Sauletekio Aleja 9, LT-2040 Vilnius, Lithuania

<sup>c</sup> Department of Biological Chemistry, Lithuanian Veterinary Academy, Tilzes Str. 18, LT-47181 Kaunas, Lithuania

Received 19 July 2005; received in revised form 21 November 2005; accepted 1 December 2005

Available online 18 January 2006

## Abstract

Vinyloxyethyl-substituted carbazole-based hydrazone and its adducts with 9-ethyl-3,6-dihydroxymethylcarbazole and 4,4'-thiobisbenzenethiol were synthesized and studied as glass-forming hole transport materials. The thermal, optical and photoelectrical properties of the synthesized materials were studied. All the synthesized compounds form glasses with the glass transition temperatures ranging from 20 to 109 °C. Their ionisation potentials established by electron photoemission technique range from 5.29 to 5.46 eV. Time-of-flight hole mobilities in the layers of the solid solutions of one synthesized hydrazone in bisphenol Z polycarbonate exceeds 10<sup>-5</sup> cm<sup>2</sup>/(V s) at high electric fields.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Hydrazone; Functional groups; Glass-forming; Hole mobility; Ionisation potential

## 1. Introduction

Aromatic hydrazones exhibit relatively high hole drift mobilities [1–3]. Some aromatic hydrazones form glasses [4–6]. One such glass-forming hydrazone exhibited very large time-of-flight hole drift mobilities, which exceeded 10<sup>-2</sup> cm<sup>2</sup>/(V s) at high electric fields [7]. In this presentation we report on the synthesis and properties of new kind of hole-transporting hydrazones, i.e. hydrazone with reactive vinyl ether functional groups. To our knowledge such glass-forming aromatic hydrazones with reactive vinyloxyethyl functional groups until now were reported only in a patent literature [8]. Such reactive aromatic hydrazones can be used for the preparation of cross-linked and therefore solvent resistant electrophotographic layers, similar to those reported earlier [9]. They also can be used as monomers for cationic polymerisation [10] and as intermediate compounds for the synthesis of larger glass-forming molecules.

It is known that molecular glasses formed by bigger molecules exhibit higher morphological stability [11]. In this presentation we demonstrate for the first time a possibility of preparation of hole transporting amorphous molecular materials by the reaction of vinyl ether with diol and dithiol. In electrophotographic photoreceptors charge-transporting compounds are usually used in the form of solid solutions in so called polymer hosts [1]. If the crystalline compounds are used as charge-transporting “guests” such systems are often morphologically unstable. Charge-transporting compounds tend to crystallize if their concentration in a polymer host exceeds 50%. To prevent this problem charge-transporting compounds that do not readily crystallize are required.

## 2. Experimental

### 2.1. Materials

The starting compound 9-ethylcarbazole 97% (Aldrich), and all the required chemicals, i.e. 2-chloroethyl vinyl ether 99% (Aldrich), *N*-phenylhydrazine 97% (Aldrich), 4,4'-thiobisbenzenethiol 98% (Aldrich), potassium carbonate 99% (Aldrich), potassium hydroxide 86% (Lachema), phospho-

\* Corresponding author. Tel.: +370 37 456525; fax: +370 37 456525.

E-mail address: [Juozas.Grazulevicius@ktu.lt](mailto:Juozas.Grazulevicius@ktu.lt) (J. Grazulevicius).

<sup>1</sup> Present address: Department of Biological Chemistry, Lithuanian Veterinary Academy, Tilzes Str. 18, LT-47181 Kaunas, Lithuania.

rus oxychloride 99% (Aldrich), *p*-toluenesulphonic anhydride 97% (Aldrich), triethylamine 99% (Acros), sodium borohydride 99% (Aldrich), sodium chloride 99% (Lachema), magnesium sulphate 97% (Aldrich), sodium sulphate 98% (Aldrich) were used as received without further purification. Organic solvents were purified and dried by the standard methods [12].

#### 2.1.1. 9-Ethylcarbazole-3-carbaldehyde (1)

POCl<sub>3</sub> (4.8 ml, 0.052 mol) was added dropwise to 5.7 ml (0.078 mol) of dry dimethylformamide (DMF) (molar ratio, 1:1.5) at 0 °C under a nitrogen atmosphere. The solution was warmed up slowly to room temperature. Then, a solution of 5.0 g (0.026 mol) of 9-ethylcarbazole in dry DMF was added dropwise to the solution of POCl<sub>3</sub> in DMF. The reaction mixture was heated at 80 °C for 24 h and then poured into ice water. The mixture obtained was neutralized with 10% solution of potassium hydroxide until the pH value of 6–8. The product was extracted with chloroform several times. The chloroform extract was dried with anhydrous sodium sulphate and filtered. The solvent was removed from the filtrate by rotary evaporator. The product 9-ethylcarbazole-3-carbaldehyde was crystallized from methanol, filtered and dried. The yield of the product C<sub>15</sub>H<sub>15</sub>N<sub>1</sub>O<sub>1</sub> (FW = 223.21) was 80% (4.57 g of grey crystals); m.p. 84.5–85 °C. IR (KBr windows) (in cm<sup>-1</sup>): ν(C–H in Ar) 3052; ν(C–H) 2973, 2894, 2822, 2745; ν(C=O) 1682; ν(C=C, C–N in Ar) 1622, 1591, 1577, 1494, 1447, 1237; γ(Ar) 807, 749, 736. MS (*m/z*): 224 (100%, *M* + 1). <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 1.42 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>); 4.31 (q, *J* = 7.0 Hz, 2H, CH<sub>2</sub>); 7.20–7.62 (m, 4H, Ar); 7.93–8.05 (d, *J* = 7.0 Hz, 1H, Ar); 8.07–8.14 (d, *J* = 7.0 Hz, 1H, Ar); 8.54 (s, 1H, Ar); 10.06 (s, 1H, CHO).

#### 2.1.2. 9-Ethylcarbazole-3,6-dicarbaldehyde (1a)

Phosphorus oxychloride (11.8 ml, 0.77 mol) was added dropwise to 67.5 g (0.92 mol) of dry DMF at 0 °C under nitrogen atmosphere. This solution was warmed up slowly to the room temperature. A solution of 15.0 g (0.077 mol) of 9-ethylcarbazole in dry DMF was added dropwise to the solution of POCl<sub>3</sub> in DMF. The reaction mixture was heated at 80 °C for 60 h and, after cooling, poured into 700 ml of ice water. The resulting mixture was neutralized with 10% potassium hydroxide solution until pH reached a value of 6–8. The precipitate was separated by filtration and washed several times with hot water. The product was purified by column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 3:1. The product was crystallized from methanol, filtered and dried. The yield of C<sub>16</sub>H<sub>15</sub>N<sub>1</sub>O<sub>2</sub> (FW = 251.22) was 60% (11.5 g of brown crystals); m.p. 146.5–148 °C. IR (KBr windows) (in cm<sup>-1</sup>): ν(C–H in Ar) 3049, 2979; ν(C–H) 2805, 2724; ν(C=O) 1682; ν(C=C in Ar) 1628, 1591, 1570, 1487; ν(C–N) 1237; γ(Ar) 828, 814. MS (*m/z*): 252 (100%, *M* + 1), 196, 145. <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 1.49 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>); 4.41 (q, *J* = 7.0 Hz, 2H, CH<sub>2</sub>); 7.47–7.55 (d, *J* = 9.0 Hz, 2H, Ar); 8.02–8.10 (d, *J* = 9.0 Hz, 2H, Ar); 8.60 (s, 2H, Ar); 8.54 (s, 1H, Ar); 10.10 (s, 2H, CHO).

#### 2.1.3. 9-Ethylcarbazole-3-carbaldehyde *N*-phenylhydrazone (2)

9-Ethylcarbazole-3-carbaldehyde (10.0 g, 0.045 mol) was dissolved in 300 ml of methanol under mild heating. Then a solution of 7.25 g (0.067 mol) of *N*-phenylhydrazine in methanol was added. The reaction mixture was refluxed for 2 h and stopped when no starting materials were left (TLC control). After cooling, yellow-grey crystals were separated by filtration, washed with a large amount of methanol and dried. The yield of C<sub>21</sub>H<sub>19</sub>N<sub>3</sub> (FW = 313.32) was 92% (13.12 g); m.p. 136–137 °C. IR (KBr windows) (in cm<sup>-1</sup>): ν(N–H) 3306; ν(C–H in Ar) 3051; ν(C–H) 2972; ν(C=C, C–N in Ar) 1602, 1494, 1475, 1237; ν(C–N) 1256; γ(Ar) 815, 747, 731. MS (*m/z*): 314 (90%, *M* + 1); 222 (100%, H<sub>5</sub>C<sub>2</sub>–C<sub>12</sub>H<sub>7</sub>N–CH=NH). <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 1.34 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>); 4.23 (q, *J* = 7.0 Hz, 2H, CH<sub>2</sub>); 6.90–7.64 (m, 8H, Ar); 7.60 (s, 1H, Ar); 7.81 (d, 1H, Ar); 8.08 (d, 2H, Ar); 8.15 (d, 1H, =CH).

#### 2.1.4. 9-Ethylcarbazole-3-carbaldehyde-*N*-(vinyloxyethyl)-*N*-phenylhydrazone (3)

9-Ethylcarbazole-3-carbaldehyde-*N*-phenylhydrazone (10.0 g, 0.031 mol) was dissolved in 50 ml of ethyl methyl ketone and then 2-chloroethyl vinyl ether (6.4 ml, 0.062 mol) was added to the solution. Then 3.5 g (0.062 mol) of KOH and 4.3 g (0.031 mol) of K<sub>2</sub>CO<sub>3</sub> were added into the reaction mixture. The second portion of KOH and K<sub>2</sub>CO<sub>3</sub> was added after 24 h. The reaction mixture was refluxed for 36 h and stopped when no starting compounds were observed (TLC control). After cooling, the inorganic components were filtered off. The solvent was removed from the filtrate by rotary evaporation. The product was purified by column chromatography using an eluent mixture of acetone and hexane in a volume ratio of 1:7. The product was crystallized from eluent, filtered and dried. The yield was 44.8% (5.47 g of yellow crystals); m.p. 106–107 °C. IR (KBr windows) (in cm<sup>-1</sup>): ν(C–H in Ar) 3051; ν(C–H) 2971, 2921, 2880; ν(C=C, C–N in Ar) 1616, 1592, 1494, 1480; ν(C–N) 1233, 1203; γ(Ar) 797, 749. MS (*m/z*): 384 (83%, *M* + 1); 224 (100%, *M* – 159); 120 (78%, C<sub>6</sub>H<sub>5</sub>–NH–N=CH<sub>2</sub>). <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 1.40 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>); 3.61–4.71 (m, 8H, N–CH<sub>2</sub>–CH<sub>2</sub>–O, N(Ar)–CH<sub>2</sub>, CH<sub>2</sub>=); 6.59 (q, *J* = 7.0 Hz, 1H, O–CH=); 6.90–7.60 (m, 9H, Ar); 7.79–8.32 (m, 3H, Ar); 8.35–8.45 (s, 1H, CH=N). Elemental analysis for C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O<sub>1</sub> (FW = 383.37): % Calc. C 78.3, H 6.5, N 10.9, O 4.1; % Found: C 78.25, H 7.02, N 10.63.

#### 2.1.5. 9-Ethyl-3,6-dihydroxymethylcarbazole

Sodium borohydride (3.82 g, 0.10 mol) was added by small portions into a solution of 8.42 g (0.0335 mol) of 9-ethylcarbazole-3,6-dicarbaldehyde in 300 ml of methanol. The reaction mixture was refluxed for 2 h and stopped when no starting compounds were observed in the reaction mixture (TLC control). After cooling the reaction mixture was poured into 800 ml of ice water. The precipitated product was separated by filtration, crystallized from methanol and dried. The yield was 43.6% (3.73 g of white-grey crystals); m.p. 143–144 °C. IR (KBr windows) (in cm<sup>-1</sup>): ν(O–H) 3323, 3233; ν(C–H in Ar) 3052; ν(C–H) 2976, 2871; ν(C=C in Ar) 1494, 1483; ν(C–N)

1236;  $\gamma(\text{Ar})$  876, 806. MS ( $m/z$ ): 238 (100%,  $M - 17(\text{OH})$ ).  $^1\text{H}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 1.27 (s, 3H,  $\text{CH}_3$ ); 4.31 (d,  $J = 8.0$  Hz, 2H,  $\text{CH}_2\text{-N}$ ); 4.72 (s, 4H,  $\text{O-CH}_2$ ); 5.19 (s, 2H, OH). Elemental analysis for  $\text{C}_{16}\text{H}_{17}\text{NO}_2$  (FW = 255.25): % Calc. C 75.26, H 6.71, N 5.49, O 12.54; % Found C 75.29, H 6.66, N 5.49.

#### 2.1.6. 9-Ethyl-3,6-di((9-ethylcarbazole-3-methylene-1-phenylhydrazinoethoxy)-1-methyl-methoxy)methyl)carbazole (**4**)

9-Ethylcarbazole-3-carbaldehyde-*N*-(vinylxyethyl)-*N*-phenylhydrazone (**3**) (1.0 g, 0.0026 mol) and 0.306 g (0.0012 mol) of 9-ethyl-3,6-dihydroxymethylcarbazole (**4**) were dissolved in 3 ml of dry tetrahydrofuran (THF) under nitrogen atmosphere. Then 1 ml of *p*-toluenesulphonic anhydride solution ( $0.5 \times 10^{-5}$  mol) in dry THF was added at the ambient temperature. The reaction mixture was stirred at  $0^\circ\text{C}$  for 18 h. Then THF was evaporated and the crude product was purified by column chromatography with an eluent mixture of hexane and acetone in a volume ratio of 7:1. The solvent was removed with a rotary evaporator. The product was dissolved in chloroform and precipitated into methanol, then filtered and dried. The yield was 19% (0.08 g of white powder). IR (KBr windows) yielded the following peaks (in  $\text{cm}^{-1}$ ):  $\nu(\text{C-H}$  in Ar) 3049, 2974;  $\nu(\text{C-H})$  2890;  $\nu(\text{C=C}$  in Ar) 1628, 1599, 1509, 1491;  $\nu(\text{C-N})$  1236;  $\nu(\text{C-O-C})$  1145;  $\gamma(\text{Ar})$  803, 748.  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.38 (m, 15H,  $\text{CH}_3$ ); 4.25 (m, 20H,  $\text{CH}_2$ , CH); 6.80–8.65 (m, 32H, Ar, =CH-). Elemental analysis for  $\text{C}_{66}\text{H}_{67}\text{N}_7\text{O}_4$  (FW = 1022.00): % Calc. C 77.56, H 6.56, N 9.60, O 6.26; % Found C 77.29, H 5.96, N 9.52.

#### 2.1.7. Di(4-(9-ethylcarbazole-3-methylene-1-phenylhydrazinoethoxy)-1-methyl-methylthio)phenyl)sulphide (**5**)

9-Ethylcarbazole-3-carbaldehyde-*N*-(vinylxyethyl)-*N*-phenylhydrazone (**3**) (3.0 g, 0.0078 mol) and 0.89 g (0.0036 mol) of 4,4'-thiobisbenzenethiol were dissolved in 10 ml of dry THF under nitrogen atmosphere. Then 2 ml of *p*-toluenesulphonic anhydride solution ( $0.5 \times 10^{-5}$  mol) in dry THF were added. The reaction mixture was stirred at  $66^\circ\text{C}$  for 15 h. Then the same portion of 4,4'-thiobisbenzenethiol was added and after 3 h the reaction was stopped since no starting materials were left in the reaction mixture (TLC control). Then THF was evaporated, and the crude product was purified by column chromatography with an eluent mixture of hexane and acetone in a volume ratio of 6:1. The solvent was removed with a rotary evaporator. The reaction product was dissolved in chloroform, precipitated into methanol, filtered and dried. The yield of the product was 30% (1.1 g of yellow powder). IR (KBr windows) (in  $\text{cm}^{-1}$ ):  $\nu(\text{C-H}$  in Ar) 3050, 2972;  $\nu(\text{C-H})$  2928, 2871;  $\nu(\text{C=C}$  in Ar) 1628, 1596, 1493;  $\nu(\text{C-O-C})$  1386;  $\nu(\text{C-N})$  1236;  $\gamma(\text{Ar})$  808, 747.  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.11–1.69 (m, 12H,  $-\text{CH}_3$ ); 3.41–4.45 (m, 14H,  $-\text{CH}_2-$ ,  $-\text{CH}-$ ); 6.79–8.32 (m, 34H, Ar, =CH-). Elemental analysis for  $\text{C}_{62}\text{H}_{60}\text{N}_6\text{S}_3\text{O}_2$  (FW = 1016.00): % Calc. C 73.29, H 5.91, N 8.27, S 9.47, O 3.15; % Found C 72.99, H 5.67, N 8.25.

## 2.2. Instrumentation

Infrared (IR) spectra were recorded using Bio-Rad Digilab FTS-40 and Perkin Elmer Spectrum GX spectrophotometers. The samples were pressed in KBr pellets.

Ultraviolet–visible (UV/vis) spectra were recorded with Spectronic Unicam Genesys<sup>TM</sup> 8 spectrophotometer.

Fluorescence emission spectra were recorded with a Hitachi MPF-4 (Japan) luminescence spectrometer.

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were obtained using a Bruker AC 250 (250 MHz), Varrian Unity Inova (300 MHz) and JOEL FX 100 (100 MHz) apparatus. All the data are given as chemical shifts in  $\delta$  (ppm), multiplicity, integration downfield from  $(\text{CH}_3)_4\text{Si}$ .

Mass spectra were obtained on a Waters ZQ (Waters, Milford, USA).

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 with a data acquisition system 414/1. Samples of  $10 \pm 0.05$  mg were put in aluminium oxide pans and heated from 30 to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Kaolin was used as a reference.

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7 calorimeter. Samples of 5–20 mg were put in aluminium pans and examined at a heating/cooling rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere.

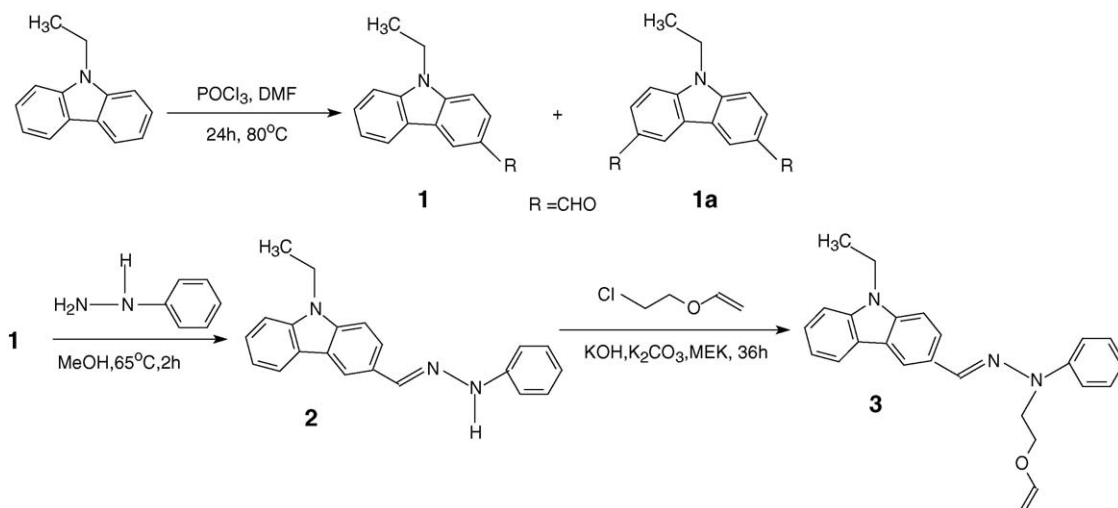
The ionisation potential ( $I_p$ ) was measured by the electron photoemission in air method as reported earlier [13]. The samples for the measurements were prepared by casting the solutions of the compounds on Al plates pre-coated with methylmethacrylate and methacrylic acid copolymer as adhesive layer.

Hole-drift mobilities were measured by a time-of-flight method in a xerographic regime [14]. The samples for the measurements were prepared by casting the solutions of the mixtures of the compounds with bisphenol Z polycarbonate (PC-Z) at mass proportion 1:1 in THF. The substrates were polyester films with Al layer.

## 3. Results and discussion

Hydrazone bearing vinylxyethyl functional (**3**) was synthesized by the multi-step synthetic route shown in Scheme 1. The first step was the formylation of 9-substituted carbazole by Vilsmeier method using  $\text{POCl}_3/\text{DMF}$  complex as a catalyst by [15] to get mono- and diformyl compounds **1** and **1a**. The second step was the condensation of aldehyde **1** with *N*-phenylhydrazine and the third step was the nucleophilic substitution reaction of 9-ethylcarbazole-3-carbaldehyde-*N*-phenylhydrazone (**2**) with 2-chloroethyl vinyl ether in the presence of KOH and  $\text{K}_2\text{CO}_3$ . The product was purified by crystallisation followed by column chromatography to obtain pure and well-defined compound.

The reactions of compound **3** with 4,4'-thiobisbenzenethiol and 9-ethyl-3,6-dihydroxymethylcarbazole, which were carried out in the presence of catalytic amount of *p*-toluenesulphonic anhydride (TSAA), lead to glass-forming hydrazone derivatives **4** and **5** (Scheme 2).

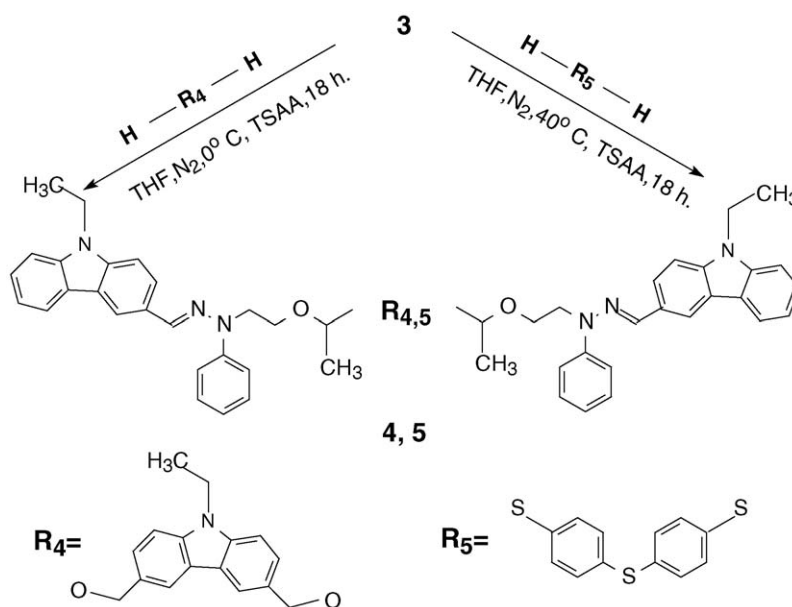


Scheme 1.

All the synthesized compounds were characterized by IR,  $^1\text{H}$  NMR and mass spectrometry and by elemental analysis. In the synthesis of hydrazone **2**, the strong IR absorption at  $1682\text{ cm}^{-1}$  due to the formyl group stretching in aldehydes **1**, **1a**, disappeared completely and two characteristic stretches of C=N group at around  $1602\text{ cm}^{-1}$  and of N–H group at  $3306\text{ cm}^{-1}$ . Hydrazones **2**, **3** have the characteristic absorption bands of aromatic groups at  $3051\text{ cm}^{-1}$  (C–H stretch) and absorption bands at  $1203\text{--}1256\text{ cm}^{-1}$  due to C–N stretching. In the synthesis of compounds **4**, **5** the characteristic IR absorption at ca.  $1386\text{ cm}^{-1}$  (C–O–C stretch) appears. IR spectra of these materials have characteristic absorption peaks of aromatic groups at  $2972\text{--}3050\text{ cm}^{-1}$  (C–H stretch),  $1492\text{--}1509$ ,  $1599$  and  $1628\text{ cm}^{-1}$  (C=C stretches) and characteristic absorption of aliphatic groups at  $2871\text{--}2890$ ,  $2928\text{ cm}^{-1}$  (C–H stretches) as well as absorption peaks

at  $747\text{--}808\text{ cm}^{-1}$  due to aromatic and heterocyclic groups stretching.

The signals of  $^1\text{H}$  NMR spectra of all the newly synthesized hydrazone compounds can be exactly assigned to the characteristic hydrogen atoms. The proton signals of the formyl group at  $10.06\text{--}10.10\text{ ppm}$  which are present in the spectra of aldehydes **1**, **1a**, disappear in the spectra of hydrazones completely. The new characteristic signals at  $8.15\text{ ppm}$  due to the protons of N=CH group appear in the spectrum of hydrazone **2**. In the spectrum of compound **3** the signals of  $\text{CH}_2$  group protons are observed at  $3.61\text{--}4.71\text{ ppm}$  and the well distinguished signal of O–CH= protons is observed at  $6.59\text{ ppm}$ . The signals at  $7.79\text{--}8.32\text{ ppm}$  can be assigned to the aromatic and heteroaromatic protons. The proton signals of –O–CH= group which appear in the spectrum of vinyloxyethyl-substituted hydrazone **3** at  $3.61\text{--}4.71\text{ ppm}$ , disappear completely in the spectra of compounds **4**, **5**. In these



Scheme 2.

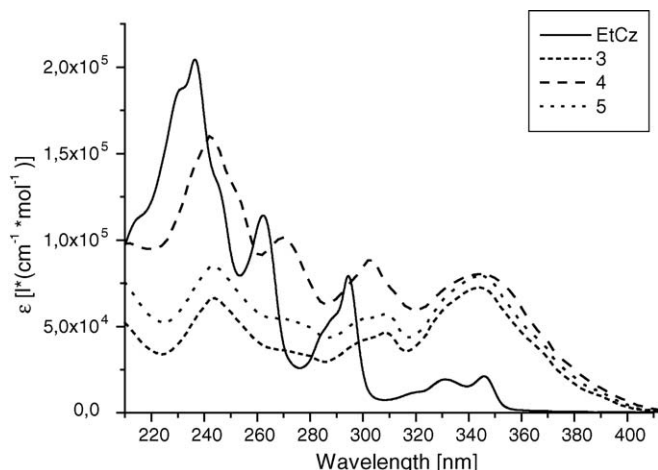


Fig. 1. UV/vis absorption spectra of dilute THF solutions ( $10^{-5}$  M) of compounds **3–5** and EtCz.

spectra the signals of  $\text{CH}_3$  group protons are at 1.11–1.69 ppm. They are considerably stepped-up compared to the spectrum of the parent hydrazone **3**. The well-distinguished signals of  $\text{CH}_2$  and CH groups protons are observed at 4.25 and 3.41–4.45 ppm in the spectra of all compounds. The signals at 6.79–8.65 ppm can be assigned to the aromatic protons.

Mass spectra of the hydrazone compounds **2**, **3** show the corresponding molecular ion peaks and peaks due to alkyl and respective aryl fragments.

Compounds **3–5** were also characterized by UV/vis spectrometry. The spectra of dilute solutions are given in Fig. 1. For the comparison the spectrum of 9-ethylcarbazole (EtCz) is given. All the synthesized hydrazones absorb in the region of 200–400 nm.

The comparison of UV absorption spectra of hydrazone **3** with the spectrum of EtCz show that the spectrum of the hydrazone is considerably red shifted with respect of the spectrum of EtCz. This observation shows, that the molecules of the hydrazones are strongly  $\pi$ -conjugated through the lone electron pair of the nitrogen atoms and that  $\pi$ -electrons are delocalised over these molecules. The UV/vis absorption spectra of compounds **4**, **5** are similar to the UV absorption spectrum of hydrazone **3**. The absorption maxima for compounds **4**, **5** are at 244, 302, and 344 nm.

The fluorescence emission spectra of the dilute THF solutions of compounds **3–5** were recorded. Their fluorescence spectra did not depend on the excitation wavelength. The emission maxima for all the compounds are given in Table 1.

The thermal behaviour of vinyloxyethyl-substituted hydrazone **3** and compounds **4** and **5** was studied by DSC and TGA. The values of glass transition temperature ( $T_g$ ), melting tem-

Table 1  
The wavelengths of fluorescence emission ( $\lambda_{\text{max}}$ ) values for compounds **3–5**

Compound	$\lambda_{\text{max}}$ (nm)
<b>3</b>	395
<b>4</b>	405
<b>5</b>	405

Table 2  
Thermal characteristics of compounds **3–5**

Compound	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$T_{\text{ID}}$ ( $^{\circ}\text{C}$ )
<b>3</b>	20	112	280
<b>4</b>	109	–	240
<b>5</b>	69	–	265

perature ( $T_m$ ) and initial decomposition temperature ( $T_{\text{ID}}$ ) are summarized in Table 2. The thermal stability of aromatic hydrazones is usually predetermined by the degradation of hydrazone moiety and does not exceed  $300^{\circ}\text{C}$  [7].  $T_{\text{ID}}$  of the reported hydrazones ranges from 240 to  $280^{\circ}\text{C}$ . The thermal stability of the twin compounds **4** and **5** depends on the origin of the linking bridge. Compound **5** containing flexible di(thiophenyl)sulphide bridge exhibit  $25^{\circ}\text{C}$  higher  $T_{\text{ID}}$  than compound **4** containing 9-ethyl-3,6-oxymethylcarbazole bridge.

Compound **3** was isolated as a crystalline material. In the DSC experiments it shows melting only in the first heating run at  $112^{\circ}\text{C}$  and forms stable glass after cooling from the melt. When the melt sample was cooled down it readily formed glass with  $T_g$  of  $20^{\circ}\text{C}$ . Compounds **4** and **5** which were isolated as amorphous materials exhibit only a glass transition and show neither melting nor crystallisation signals in the first and the following heating cycles of DSC.  $T_g$  of these twin compounds depends on the linking bridge.  $T_g$  of di(thiophenyl)sulphide-bridged compound **5** is considerably lower than that of 9-ethyl-3,6-oxymethylcarbazole-bridged compound **4**.

All the synthesized hydrazones are soluble in common organic solvents such as chloroform, acetone, THF. The values of ionisation potentials ( $I_p$ ) of their amorphous films are given in Table 3. They range from 5.29 to 5.46 eV.

The highest ionisation potential was observed for monohydrazone **3**. The relatively low values of  $I_p$  make these compounds useful for the application in electrophotographic photoreceptors. Holes would be injected easily into the layers of these materials from charge generation layers widely used in electrophotographic photoreceptors. The  $I_p$  values of charge generation materials used in electrophotographic photoreceptors such as titanil phthalocyaniones, perylene pigments and bisazo pigments are in the range of 5.1–5.6 eV [16].

The origin of the linking bridge of the twin molecules influences also the values of  $I_p$  of these materials. 9-Ethyl-3,6-oxymethylcarbazole-bridged compound **4** exhibit slightly lower ionisation potential than the corresponding di(thiophenyl)sulphide-bridged compound. The electron photoemission spectrum of the film of compound **4** is shown in Fig. 2. By the straight lines with the different slopes the photoemission spectrum can be divided into two parts corresponding

Table 3  
Ionisation potentials of the films of hydrazones **3–5**

Compound	$I_p$ (eV)
<b>3</b>	5.46
<b>4</b>	5.29
<b>5</b>	5.39

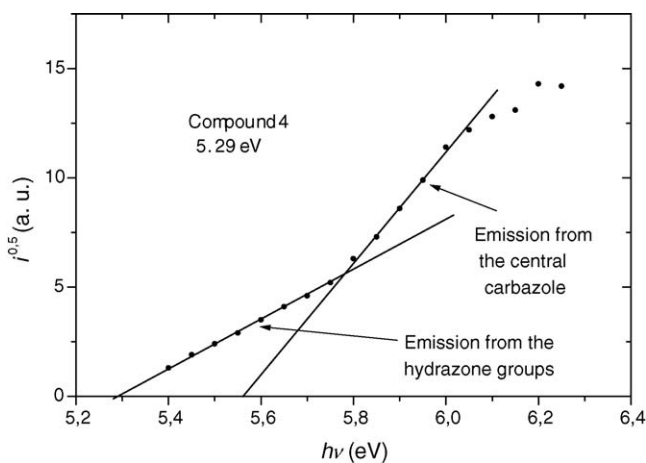


Fig. 2. Electron photoemission spectrum of compound 4.

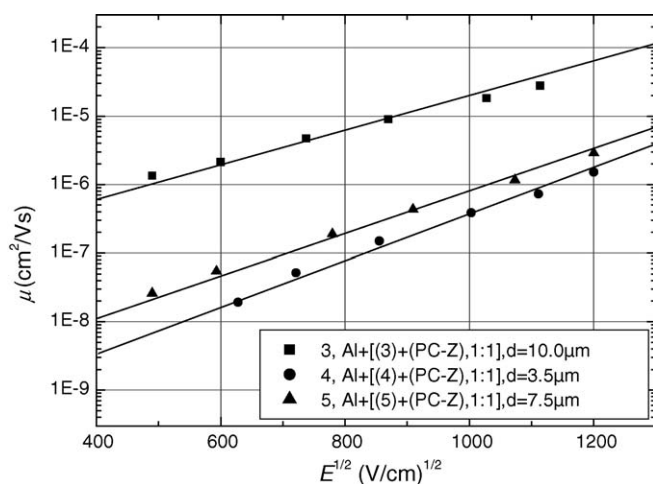


Fig. 3. Electric field dependencies of holes drift mobilities in the amorphous films of 50% solid solutions of compounds 3–5 in PC-Z at 22 °C.

to the photoemission from hydrazone moiety and to the photoemission from the carbazole moiety.

Fig. 3 shows the electric field dependencies of hole drift mobilities in the solid solutions of vinyloxyethyl-substituted hydrazone 3 and amorphous compounds 4 and 5 in PC-Z. The linear dependencies of hole drift mobilities on the square root of electric field were observed for all the samples.

The highest hole drift mobilities were observed for the solid solutions of compound 3. Hole drift mobilities in this system exceeds  $10^{-5} \text{ cm}^2/(\text{V s})$  at a high electric field and it is by ca. one order of magnitude higher than those observed in the systems containing twin compounds 4 and 5. These are relatively high charge mobilities as for molecularly doped polymers. In

the amorphous films of pure charge transport materials charge mobilities are usually by one to two orders of magnitude higher than in molecularly doped polymers containing 50% of active material [1].

In conclusion vinyloxyethyl-substituted carbazole-based hydrazone and its adducts with 9-ethyl-3,6-dihydroxymethylcarbazol and 4,4'-thiobisbenzenethiol were synthesized and studied as glass-forming hole transport materials. The thermal, optical and photoelectrical properties of the synthesized materials were studied. All the synthesized compounds form glasses with the glass transition temperatures ranging from 20 to 109 °C. Their ionisation potentials established by electron photoemission technique range from 5.29 to 5.46 eV. The time-of-flight hole mobilities in the layers of the solid solutions of vinyloxyethyl-substituted hydrazone in PC-Z exceed  $10^{-5} \text{ cm}^2/(\text{V s})$  at high electric fields.

### Acknowledgements

This research was supported by Samsung Electronics and Lithuanian Science and Studies Foundation. Dr. Habil. V. Gaidelis is thanked for the ionisation potential measurements.

### References

- [1] P.M. Borsenberger, D.S. Weiss, *Organic Photoreceptors for Xerography*, Dekker, New York, 1998, 768 pp.
- [2] P.M. Borsenberger, *Adv. Chem. Mater. Opt. Electron.* 1 (1992) 73–80.
- [3] S. Nomura, K. Nishimura, Y. Shiota, *Mol. Cryst. Liq. Cryst.* 313 (1998) 247–252.
- [4] K. Nishimura, T. Kobota, H. Inada, Y. Shiota, *J. Mater. Chem.* 1 (1991) 897–899.
- [5] K.J. Jiang, Y.L. Sun, K.F. Shao, L.M. Yang, *Chem. Lett.* 33 (2004) 50–51.
- [6] R. Lygaitis, J.V. Grazulevicius, V. Gaidelis, V. Jankauskas, J. Sidaravicius, Z. Tokarski, N. Jubran, *Mol. Cryst. Liq. Cryst.* 427 (2005) 407–418.
- [7] J. Ostrauskaite, V. Voska, J. Antulis, V. Gaidelis, V. Jankauskas, J.V. Grazulevicius, *J. Mater. Chem.* 12 (2002) 3469–3474.
- [8] J.V. Grazulevicius, G. Buika, V. Jankauskas, V. Gaidelis, R. Budreckiene, Z. Tokarski, N. Jubran, *US Patent Application 2005/0095517* (2005).
- [9] V. Gaidelis, J. Gavutienė, V. Getautis, J.V. Grazulevicius, V. Jankauskas, R. Kavaliunas, R. Lazauskaite, O. Paliulis, R. Rossman, D.J. Sidaravicius, T.P. Smith, A. Stanishauskaitė, *US Patent 6,214,503* (2001).
- [10] T. Hashimoto, K. Ishizuka, A. Umehara, T. Kodaira, *J. Polym. Sci., Part A: Polym. Chem.* 40 (2002) 4053–4064.
- [11] Y. Shiota, *J. Mater. Chem.* 15 (2005) 75–93.
- [12] L.M. Harwood, C.J. Moody, in: O. Mead (Ed.), *Organic Chemistry, Principles and Practice*, Blackwell Science, 1989.
- [13] S. Grigalevicius, J.V. Grazulevicius, V. Gaidelis, V. Jankauskas, *Polymer* 43 (2002) 2603–2608.
- [14] Y. Archie, C. Chan, C. Juhasz, *Int. J. Electron.* 62 (4) (1987) 625–631.
- [15] E.E. Campaigne, W.L. Archer, *Org. Synth.* 4 (1953) 27–29.
- [16] S. Grigalevicius, G. Blazys, J. Ostrauskaite, J.V. Grazulevicius, V. Gaidelis, V. Jankauskas, E. Montrimas, *Synth. Met.* 128 (2002) 127–131.