

# Synthesis and properties of new glass-forming compounds with donor and acceptor moieties

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Novel bipolar molecules containing electron-accepting (trioxothioxanthene, benzotriazole, trinitrophenol) and electron-donating (carbazole) moieties were synthesized and characterized by nuclear magnetic resonance, infrared spectroscopy, ultraviolet spectroscopy and mass spectrometry. Two synthesized compounds, 6-(9H-carbazole) hexyl 9,10,10-trioxo-9H-thioxanthen-3-oate and 1-(9H-carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol, form glasses with glass transition temperatures of 45 °C and 59 °C respectively as established by differential scanning calorimetry. The ionisation potentials of films of these compounds measured by the electron photoemission technique are 5.77 eV and *ca.* 6 eV, respectively.

**Key words:** trioxothioxanthene, benzotriazole, trinitrophenol, carbazole, bipolar, glass-forming materials, ionisation potential

## INTRODUCTION

Bipolar molecular glasses are of great interest in organic light-emitting diodes (OLEDs). Due to imbalanced charge injection and transport, charge recombination in thin film OLEDs often occurs close to metal electrode, and luminescence quenching by the metal results in a lower device efficiency [1]. To achieve a balanced charge injection and transport, compounds containing both electron transport segments and hole transport segments are of interest for the application in OLEDs. In this presentation we report on the synthesis and properties of novel compounds containing both donor (carbazole) and acceptor (trioxothioxanthene, trinitrophenol, benzotriazole) units.

## EXPERIMENTAL

### Materials

9,10,10-Trioxo-9H-3-thioxanthenecarboxylic acid, 1,6-dibromohexane, 1-H-benzotriazole were purchased from Aldrich and used as received without further

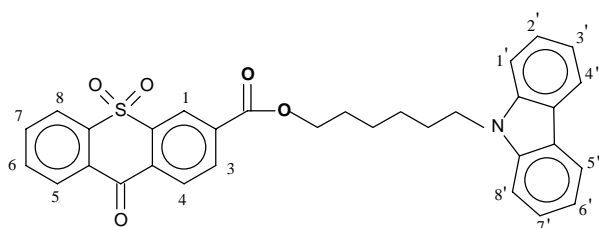
purification. 9-H-carbazole, 2,4,6-trinitrophenol, potassium fluoride were purchased from Reakhim (Russia). 9-(2-oxiranylmethyl)-9H-carbazole was obtained from Biolar (Latvia).

**6-Bromohexyl-9H-carbazole (a).** 4.31 g (25.8 mmol) of 9H-carbazole, 51.6 g (250.8 mmol) of 1,6-dibromohexane and 0.159 g (0.468 mmol) of tetrabutylammonium hydrogen sulphate were dissolved in 2-butanone (100 ml). 2.89 g (25.8 mmol) of potassium hydroxide was added stepwise and the reaction mixture was refluxed for 12 h. Then unreacted potassium hydroxide and inorganic salts were removed from the reaction mixture by filtration. The solvent was removed by rotary evaporation and unreacted 1,6-dibromohexane was distilled under reduced pressure. The crude product was re-crystallized from ethanol to give 5.4 g (63%) of white crystals (m.p. 45 °C). <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm) 1.1–1.65 (m, 4H, 2CH<sub>2</sub>), 1.65–2.05 (m, 4H, 2CH<sub>2</sub>), 3.33 (t, 2H, *J* = 6.5 Hz, BrCH<sub>2</sub>), 4.28 (t, 2H, *J* = 7.1 Hz, NCH<sub>2</sub>), 7.1–7.6 (m, 6H, ar), 8.08 (d, 2H, *J* = 7.5 Hz, ar). IR (in KBr), ν/cm<sup>-1</sup>: 3050 (CH<sub>ar</sub>), 2940, 2860 (CH<sub>aliphatic</sub>), 1600, 1460 (C = C<sub>ar</sub>), 1330 (C-N).

**6-(9H-Carbazole)hexyl 9,10,10-trioxo-9H-thioxanthen-3-oate (I).** To the magnetically stirred solu-

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tion of 0.425 g (1.86 mmol) of 9,10,10-trioxo-9H-3-thioxanthenecarboxylic acid in DMF 0.238 g (4.09 mmol) of potassium fluoride was added. Then after several minutes 0.614 g (1.86 mmol) of 6-bromohexyl-9H-carbazole (**a**) was added. The reaction mixture was heated to 90 °C and stirred for 24 h. After recooling to the room temperature it was poured into water. The precipitated crude product was filtered and purified by silica gel column chromatography (eluent acetone / n-hexane = 1:2). After re-crystallization from the mixture of acetone and hexane (1:2) 0.467 g (47%) of yellow crystals was obtained (m.p.: 107 °C). FW = 537.28 g/mol.



<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, δ, ppm): 1.49–1.52 (m, 4H, 2CH<sub>2</sub>), 1.79 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>-), 1.94 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>-), 4.36 (m, 4H, NCH<sub>2</sub>, OCH<sub>2</sub>), 7.19–7.32 (m, 2H, 1',8'-H), 7.39–7.54 (m, 4H, 2',3',6',7'-H), 7.79–7.99 (m, 2H, 6',7'-H), 8.11 (d, 2H, J = 7.8Hz, 4',5'-H), 8.22 (d, 1H, J = 8Hz, 5-H), 8.3–8.45 (m, 3H, 3,4,8-H), 8.81 (s, 1H, 1-H). IR (in KBr), v/cm<sup>-1</sup>: 3050 (CH<sub>ar</sub>), 2925, 2850 (CH<sub>aliphatic</sub>), 1720 (C = O), 1660 (C = O), 1600, 1590, 1460 (C = C<sub>ar</sub>), 1400 (CO), 1300 (SO<sub>2</sub>), 1270 (SO<sub>2</sub>), 1220 (C-N), 1140 (SO<sub>2</sub>), 730 (CH<sub>ar</sub>), 710 (CH<sub>ar</sub>). MS (70 eV): m/z = 537 (M<sup>+</sup>), 180.

**9-(6-Benzotriazol-1-yl-hexyl)-9H-carbazole (2).** 1.174 g (9.84 mmol) of 1H-benzotriazole, 2.71 g (8.2 mmol) of 6-bromohexyl-9H-carbazole (**a**) were dissolved in acetone. Then 2.105 g (15.25 mmol) of potassium carbonate was added stepwise and the reaction mixture was refluxed for 7 h. Then unreacted potassium carbonate and inorganic salts were removed from the reaction mixture by filtration. The solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography (eluent ethyl acetate / n-hexane = 1:3) to yield 1.8 g (83%) of a viscous resin (FW = 368.23 g/mol). <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 1.1–1.45 (m, 4H, 2CH<sub>2</sub>), 1.55–1.97 (m, 4H, 2CH<sub>2</sub>), 4.23 (t, 2H, J = 6.8Hz, NCH<sub>2</sub>-), 4.5 (t, 2H, J = 7.3Hz, NCH<sub>2</sub>-), 6.95–7.5 (m, 8H, ar), 7.83–8.1(m, 4H, ar). IR (in KBr), v/cm<sup>-1</sup>: 3080 (CH<sub>ar</sub>), 2950 (CH<sub>aliphatic</sub>), 1600, 1465 (C = C<sub>ar</sub>), 1220 (C-N), 720 (CH<sub>ar</sub>). MS (70 eV): m/z = 368(M<sup>+</sup>), 180, 133, 77.

**1-(9H-Carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol (3).** 2.06 g (9.22 mmol) of 9-(2-oxiranilylmethyl)-9H-carbazole and 1.07 g (4.66 mmol) of 2,4,6-tri-

nitrophenol were placed into a round bottom flask. The reaction mixture was heated to 130 °C and stirred for 3 h under a nitrogen atmosphere. Then the hot reaction mixture was dissolved in ethyl acetate. n-Hexane was added to the solution to remove the polymeric byproduct. A red solution was obtained, and it was washed with a sodium hydroxide solution to remove 2,4,6-trinitrophenol. The solvent was evaporated and the crude product was dissolved in a small amount of chloroform. After crystallization, filtration and drying in vacuum 0.83 g (39%) of red fine crystals (m.p.: 181 °C) were obtained. FW = 452.38 g/mol. <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 2.77 (s, 1H, -OH), 4.13–4.77 (m, 5H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 7.1–7.78 (m, 5H, ar), 8.13 (d, 2H, ar), 9.1 (s, 2H, Ph). IR (in KBr), v/cm<sup>-1</sup>: 3520 (OH), 1600 (C = C<sub>ar</sub>), 1340, 1540 (NO<sub>2</sub>), 720 (CH<sub>ar</sub>). MS (70 eV): m/z = 453 (M<sup>+</sup>+1), 224, 180.

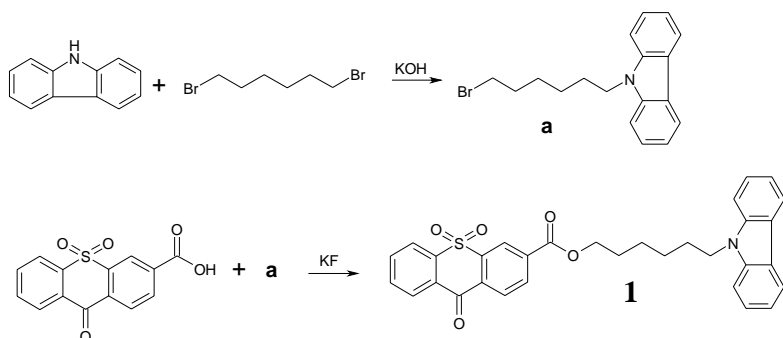
## METHODS

Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC-7 and STAR<sup>e</sup>-7 differential scanning calorimeters. Thermogravimetric analysis (TGA) was fulfilled using NETZSCH STA 409 thermogravimeter. IR-spectroscopy was performed on Specord 75 IR and Perkin Elmer 1330 IR, using KBr pellets. <sup>1</sup>H NMR spectra were obtained on Bruker AC 250 (250 MHz), and JOEL JNM-FX 100 (100MHz) instruments. Mass spectra were obtained on a Varian MAT-312 spectrometer. UV-VIS spectra were recorded with Hitachi U3000 and Specord M-40 spectrometers.

The ionisation potentials (I<sub>p</sub>) of the films of the synthesized compounds were measured by the method of electron photoemission in air as described before [2, 3]. 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 the adhesive layer.

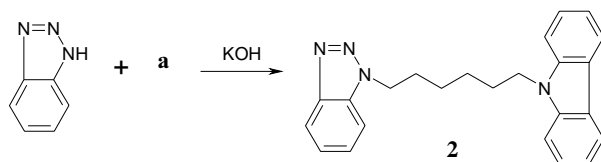
## RESULTS AND DISCUSSION

Compound **1** was synthesized in the synthetic route shown in Scheme 1. The first step was alkylation of 9H-carbazole with 1,6-dibromohexane using potassium hydroxide in the presence of tetrabutylammonium hydrogen sulphate as a phase transfer catalyst. The second step was esterification of 9,10,10-trioxo-9H-3-thioxanthenecarboxylic acid using 6-bromohexyl-9H-carbazole (**a**) in the presence of potassium fluoride in DMF. The reaction was controlled by thin layer chromatography and proceeded until the starting bromide was fully exhausted.



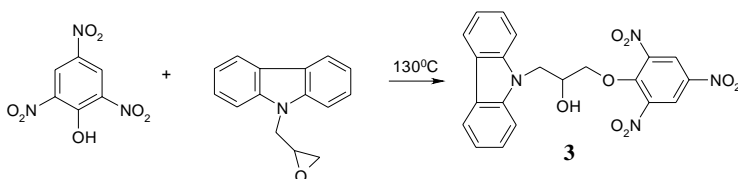
**Scheme 1.** Synthetic route to compound **1**

9-(6-Benzotriazol-1-yl-hexyl)-9H-carbazole **2** was synthesized by alkylation of 1H-benzotriazole with 6-bromo-hexyl-9H-carbazole (**a**) in the presence of potassium carbonate (Scheme 2). The product was purified by column chromatography to yield 83% of the pure compound.



**Scheme 2.** Synthesis of compound **2**

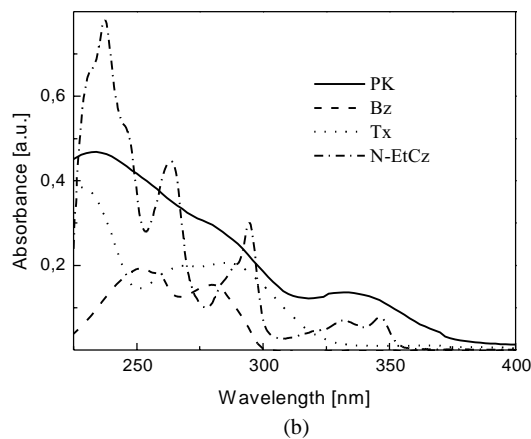
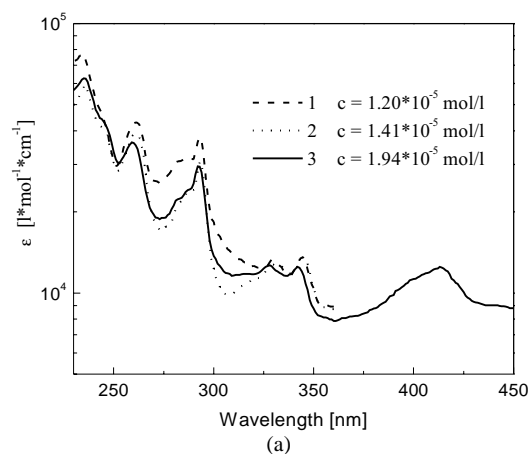
It is known that electron-accepting trinitrophenol moiety can provide good electron-transporting properties. Vannikov et al. [3] reported that N-picrylamine derivatives show electron drift mobilities of  $10^{-4}$  cm<sup>2</sup>/(Vs) at electric fields of the order of  $10^5$  V/cm. On the other hand, it is widely known that electron-donating carbazole moiety provides an effective hole transport. To combine these two moieties in one molecule, we have synthesized 1-(9H-carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol (**3**). Compound **3** was prepared by the reaction of 2,4,6-trinitrophenol and 9-(2-oxiranylmethyl)-9H-carbazole (Scheme 3). The reaction was carried out in melt. The melting points of the starting materials are 122 °C and 112 °C respectively, therefore the reaction was carried out at 130 °C. After heating the reaction mixture for 3 h the yield of 39% of **3** was reached.



**Scheme 3.** Synthesis of 1-(9H-carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol (**3**)

The chemical structures of the newly synthesized compounds (**1**, **2**, **3**) were confirmed by <sup>1</sup>H NMR, IR, spectroscopy and mass spectrometry. These compounds are soluble in common organic solvents such as chloroform, acetone, tetrahydrofuran (THF).

Figure 1a shows UV spectra of the dilute solutions of the compounds synthesized. Absorption spectra of compounds **1** and **2** closely resemble the sum of the spectra of the elec-



**Fig. 1.** UV absorption spectra of dilute solutions of compounds **1**, **2**, **3** (a) and of the model compounds (b): N-ethylcarbazole (N-EtCz), 1H-benzotriazole (BT), 2,4,6-trinitrophenol (TNTP), 9,10,10-trioxo-9H-3-thioxanthene-carboxylic acid (TOTC) in THF ( $10^{-5}$  mol/l)

tron accepting chromophores (trioxothioxanthene, benzotriazole) and N-ethylcarbazole (Fig. 1b) indicating that the interaction between the two chromophores is relatively weak in dilute solution, so that it only slightly changes the energetic positions of the ground and excited states of the individual chromophores. The new absorption band at 413 nm, which is cha-

racteristic neither of the spectrum of N-ethylcarbazole nor of the spectrum of trinitrophenol, is observed in the UV spectrum of compound **3**. This observation shows that formation of an intermolecular charge transfer complex between the electron donating (carbazole) and electron accepting (trinitrophenol) chromophores occurs in a dilute THF solution of **3**. Such complexes are formed through the donor:acceptor linkage, when the electron hops from the highest occupied molecular orbit of the donor to the lowest unoccupied molecular orbit of the acceptor [4]. The energy of the system becomes lower when the jump of the electron occurs and a new band, shifted to the longer wavelengths, appears in the electronic spectrum as a result of the donor–acceptor interaction.

Thermal investigations of the newly synthesized compounds were performed by TGA and DSC. The values of glass transition temperature ( $T_g$ ), melting point ( $T_m$ ) and 5% weight loss temperature ( $T_{ID}$ ) are summarized in Table 1. TGA has revealed a high thermal stability of compound **1**. Its 5% weight loss temperature ( $T_{ID}$ ) is 356 °C. The first DSC heating runs of compounds **1** and **3** have revealed melting peaks with the maxima at 112 °C and 194 °C, respectively. Re-cooling revealed no crystallization peaks, and only glass transition was observed in the second DSC heating runs at 45 °C and 59 °C, respectively. 9-(6-Benzotriazol-1-yl-hexyl)-9H-carbazole (**2**) was isolated as a viscous resin, and we can only state that its glass transition temperature is below the room temperature.

Table 1. DSC and TGA data on compounds **1**, **3**

Compound	$T_g$ , [°C]	$T_m$ , [°C]	$T_{ID}$ , [°C]
<b>1</b>	45	112	356
<b>3</b>	59	194	229

An important characteristic of electronically active compounds used in optoelectronic devices is the ionisation potential ( $I_p$ ), which characterizes the electron releasing work under illumination. The  $I_p$  values for the films of the synthesized compounds were established by the electron photoemission technique from the dependencies of photocurrent ( $I$ ) on the incident light quanta energy, which are named as electron photoemission spectra and plotted as  $I^{0.5} = f(h\nu)$ . Usually the dependence of the photocurrent on incident light quanta energy is well described by this relationship near the threshold. The linear part of this dependency is extrapolated to the  $h\nu$  axis and the  $I_p$  value is determined as the photon energy at the interception point. The photoe-

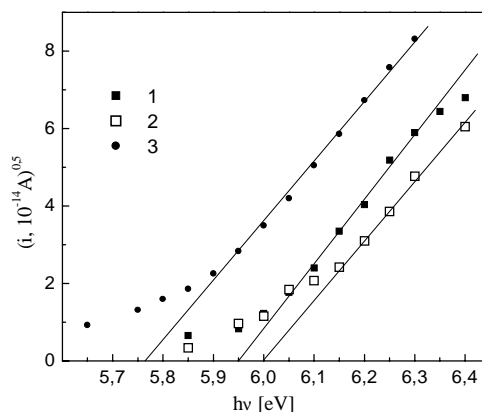


Fig. 2. Photoemission spectra of amorphous films of compounds **1**, **2**, **3**

mission spectra of the amorphous films of compounds **1**, **2**, **3** measured at 25 °C are shown in Fig. 2.

The values of ionisation potentials of thin films of the synthesized bipolar compounds are presented in Table 2. For comparison, the value of ionisation potential of carbazole-containing oligoether poly[9-(2,3-epoxypropylcarbazole)] (PEPK) is given [5]. The  $I_p$  value of compound **3** is very close to that of PEPK. This observation shows that probably the interaction between electron accepting and donating chromophores is rather weak in the solid state. The  $I_p$  of compounds **1** and **2** is higher than that of PEPK, which means that in the solid state there is an interaction between the carbazolyl and electron-accepting groups. Only an approximate value of  $I_p$  was obtained for the film of **2**. Ionisation potentials higher than *ca.* 6 eV can be measured only in vacuum, because air absorbs the light needed for the measurements. The photoemission spectrum of compound **2** only begins to appear at the spectral limit of the method used.

Table 2. Ionisation potentials of compounds **1**, **2**, **3**

Compound	<b>1</b>	<b>2</b>	<b>3</b>	PEPK
$I_p$ , [eV]	5.97	~6	5.77	5.86

## CONCLUSIONS

Three new compounds containing acceptor and donor moieties were synthesized and studied. 6-(9H-Carbazole) hexyl 9,10,10-trioxo-9H-thioxanthene-3-oate and 1-(9H-carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol form glasses with glass transition temperatures of 45 °C and 59 °C respectively as established by differential scanning calorimetry. The optical properties of the dilute solutions of the compounds synthesized were studied. Absorption spec-

tra of 6-(9H-carbazole) hexyl 9,10,10-trioxo-9H-thioxanthen-3-oate and 9-(6-Benzotriazol-1-yl-hexyl)-9H-carbazole closely resemble the sum of the spectra of the electron accepting and donating chromophores. The UV spectrum of dilute solution of 1-(9H-carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol shows the existence of charge transfer interaction between the electron-accepting and electron-donating chromophores of this molecule. The absorption band of the complex is observed at 413 nm. The ionisation potentials of the films of these compounds measured by the electron photoemission technique range from 5.77 eV to *ca.* 6 eV.

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#### NAUJŲ DONORINES IR AKCEPTORINES GRUPES TURINČIŲ MAŽAMOLEKULIŲ STIKLŲ SINTEZĖ IR SAVYBĖS

##### S a n t r a u k a

Susintetinti nauji junginiai, turintys akceptorinius (trioksotioksanteno, benzotriazolo, trinitrofenolio) ir donorinius (karbazolo) fragmentus. Branduolių magnetinio rezonanso, masių spektrometrijos ir infraraudonosios spektroskopijos metodais identifikuota jų struktūra.

Diferencinės skenuojamosios kalorimetrijos metodu nustatyta, kad 6-(9H-karbazol) heksil 9,10,10-trioksotioksanten-3-oatas ir 1-(9H-karbazolil)-3-(2,4,6-trinitrofenoksi)-2-propanolis sudaro stiklus, kurių stiklėjimo temperatūra yra atitinkamai 45 ir 59°C. Susintetintų junginių optinių savybių tyrimai parodė, jog 1-(9H-karbazolil)-3-(2,4,6-trinitrofenoksi)-2-propanolio molekulėje egzistuoja elektronakceptorinės ir elektrondonorinės dalių sąveika. Šio junginio UV spektrui būdinga absorbcijos juosta ties 413 nm, kurios nėra nei 9-etilkarbazolo, nei 2,4,6-trinitrofenolio spektruose. 6-(9H-karbazol) heksil 9,10,10-trioksotioksanten-3-oato bei 9-(6-benzotriazol-1-il-heksil)-9H-karbazolo UV spektruose donorinė-akceptorinė sąveika neatsispindi. Elektronų fotoemisijos metodu nustatyti susintetintų junginių jonizacijos potencialai išsidėsto nuo 5,77 iki 6 eV.