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Synthesis and photophysical properties of bipolar low-molar-mass amorphous materials

R. Lygaitis[a], A. Matoliukstyte[a], N. Kreiveniene[b], J.V. Grazulevicius[a,*]

[a] *Department of Organic Technology, Kaunas University of Technology, Radvil n pl. 19, LT-3028 Kaunas, Lithuania*
[b] *Department of Inorganic Chemistry, Kaunas University of Technology, Radvil n pl. 19, LT-3028 Kaunas, Lithuania*

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Abstract

Bipolar molecules containing electron-accepting (trioxothioxanthene, benzotriazole, trinitrophenol) and electron-donating (carbazole) moieties were synthesised and characterised by nuclear magnetic resonance, infrared spectroscopy, and mass spectrometry. The thermal, optical and photoelectrical properties of the synthesised compounds are reported. Two synthesised 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 above room temperature i.e. 45 and 59 °C, respectively, as established by differential scanning calorimetry. The ionisation potentials of these compounds measured by electron photoemission technique are 5.77 and ca. 6 eV, respectively.

Keywords: Trioxothioxanthene; Benzotriazole; Trinitrophenol; Carbazole; Bipolar; Glass-forming; Ionisation potential

1. Introduction

Bipolar molecular glasses are of interest for the application organic light-emitting diodes (OLEDs). Due to imbalanced charge injection and transport, the charge recombination in thin films of OLEDs often occurs close to metal electrode and luminescence quenching by the metal results in lower device efficiency [1]. For the achievement of the balanced charge injection and transport compounds containing both electron transport moieties and hole transport segments are of interest. In this presentation, we report on the synthesis and properties of novel compounds containing both donor (carbazole) and acceptor (trioxothioxanthene, trinitrophenol, benzotriazole) moieties. We have chosen these moieties as the building blocks in the design and synthesis of the bipolar compounds for the following reasons. It is widely known, that electron-donating carbazole moiety provides effective hole transport both in polymers and low-molar-mass materials [2]. On the other hand it is also known that electron-accepting trinitrophenol moiety can provide good electron-transporting properties. Tameev et al. [3] reported on molecularly doped polymer containing only 10 wt.% of *N*-picrylamine derivatives show electron drift mobilities of 10^{-4} cm^2/V s at an electric fields of the order of 10^5 V/cm. Trioxothioxanthene moiety is widely used in the synthesis of organic electron-transporting compounds, especially those designed for electrophotographic photoreceptors [4] and photorefractive materials [5,6]. Benzotriazole derivatives are also known as electron-transporting materials [7].

2. Experimental

2.1. Materials

9,10,10-Trioxo-9H-3-thioxanthenecarboxylic acid, 1,6-dibromohexane, 1H-benzotriazole were purchased from “Aldrich” and used as received without further purification. 9H-carbazole, 2,4,6-trinitrophenol, potassium fluoride were purchased from “Reakhim” (Russia). 9-(2-Oxiranylmethyl)-9H-carbazole was obtained from “Biolar” (Latvia).

2.1.1. 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 were added stepwise and the reaction mixture was

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[*] Corresponding author. Tel.: +370-37-456525; fax: +370-37-456525.
E-mail address: juogra@ctf.ktu.lt (J.V. Grazulevicius).

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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-crystallised from ethanol to give 5.4 g (63%) of white crystals (mp 45 °C). ^{1}H NMR (100 MHz, $CDCl_3$, δ, ppm): 1.1–1.65 (m, 4H, $2CH_2$), 1.65–2.05 (m, 4H, $2CH_2$), 3.33 (t, 2H, $J = 6.5$ Hz, $BrCH_2$), 4.28 (t, 2H, $J = 7.1$ Hz, NCH_2), 7.1–7.6 (m, 6H, ar), 8.08 (d, 2H, $J = 7.5$ Hz, ar). IR (in KBr), ν/cm^{-1}: 3050 (CH_{ar}), 2940, 2860 ($CH_{aliphatic}$), 1600, 1460 ($C{=}C_{ar}$), 1330 (C–N).

*2.1.2. 6-(9H-Carbazole)hexyl 9,10,10-trioxo-9H-thioxanthen-3-oate (**1**)*

To the magnetically stirred solution 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 were added. Then after several minutes 0.614 g (1.86 mmol) of 6-bromohexyl-9H-carbazole (**a**) were added. The reaction mixture was heated to 90 °C and stirred for 24 h. After re-cooling 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-crystallisation from the mixture of acetone and hexane (1:2) 0.467 g (47%) of yellow crystals were obtained (mp: 107 °C) (FW $=$ 537.28 g/mol). ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 1.49–1.52 (m, 4H, $2CH_2$), 1.79 (m, 2H, $OCH_2C\mathbf{H_2}$), 1.94 (m, 2H, $NCH_2C\mathbf{H_2}$), 4.36 (m, 4H, NCH_2, OCH_2), 7.19–7.32 (m, 2H, Ht), 7.39–7.54 (m, 4H, Ht), 7.79–7.99 (m, 2H, Ht), 8.11 (d, 2H, $J = 7.8$ Hz, Ht), 8.22 (d, 1H, $J = 8$ Hz, Ht), 8.3–8.45 (m, 3H, Ht), 8.81 (s, 1H, Ht). IR (in KBr), ν/cm^{-1}: 3050 (CH_{ar}), 2925, 2850 ($CH_{aliphatic}$), 1720 (C=O), 1660 (C=O), 1600, 1590, 1460 ($C{=}C_{ar}$), 1400 (CO), 1300 (SO_2), 1270 (SO_2), 1220 (C–N), 1140 (SO_2), 730 (CH_{ar}), 710 (CH_{ar}). MS (70 eV): $m/z = 537$ (M^{+}), 180.

*2.1.3. 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 were 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). ^{1}H NMR (100 MHz, $CDCl_3$, δ, ppm): 1.1–1.45 (m, 4H, $2CH_2$), 1.55–1.97 (m, 4H, $2CH_2$), 4.23 (t, 2H, $J = 6.8$ Hz, NCH_2), 4.5 (t, 2H, $J = 7.3$ Hz, NCH_2), 6.95–7.5 (m, 8H, ar), 7.83–8.1 (m, 4H, ar). IR (in KBr), ν/cm^{-1}: 3080 (CH_{ar}), 2950 ($CH_{aliphatic}$), 1600, 1465 ($C{=}C_{ar}$), 1220 (C–N), 720 (CH_{ar}). MS (70 eV): $m/z = 368$ (M^{+}), 180, 133, 77.

*2.1.4. 1-(9H-Carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol (**3**)*

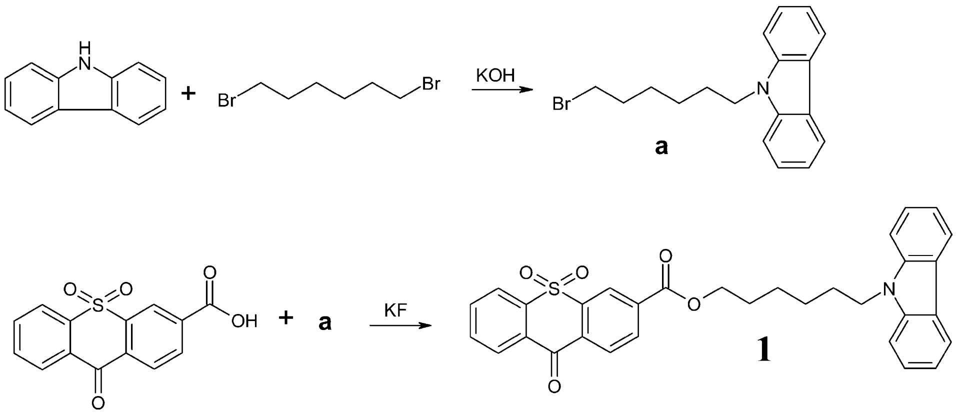
2.06 g (9.22 mmol) of 9-(2-oxiranylmethyl)-9H-carbazole and 1.07 g (4.66 mmol) of 2,4,6-trinitrophenol were placed into a round bottom flask. The reaction mixture was heated to 130 °C and stirred for 3 h under nitrogen atmosphere. Then the hot reaction mixture was dissolved in ethyl acetate. n-Hexane was added to the solution to remove the polymeric by-product. The red solution was obtained. It was washed with solution of sodium hydroxide in water to remove 2,4,6-trinitrophenol. The solvent was evaporated and the crude product was dissolved in a small amount of chloroform. After crystallisation, filtration and drying in vacuum 0.83 g (39%) of red fine crystals (mp: 181 °C) were obtained (FW $=$ 452.38 g/mol). ^{1}H NMR (100 MHz, $CDCl_3$, δ, ppm): 2.77 (s, 1H, OH), 4.13–4.77 (m, 5H, OCH_2CHCH_2N), 7.1–7.78 (m, 5H, ar), 8.13 (d, 2H, ar), 9.1 (s, 2H, Ph). IR (in KBr), ν/cm^{-1}: 3520 (OH), 1600 ($C{=}C_{ar}$), 1340, 1540 (NO_2), 720 (CH_{ar}). MS (70 eV): $m/z = 453$ ($M^{+} + 1$), 224, 180.

3. Methods

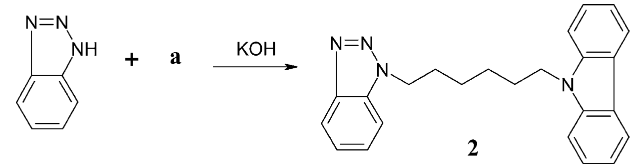
Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC-7 and STAR^{e}-7 differential scanning calorimeters. Thermogravimetric analysis (TGA) was fulfilled using NETZSCH STA 409 thermogravimeter. IR-spectroscopy was performed on Specord 75 IR and Perkin-Elmer 1330 IR, using KBr pellets. ^{1}H NMR spectra were obtained on Bruker AC 250 (250 MHz), BMR Avanse 250 (250 MHz) and JOEL JNM-FX 100 (100 MHz) instruments. Mass spectra were obtained on Varian MAT-312 spectrometer. UV-Vis spectra were recorded with Hitachi U3000 and Specord M-40 spectrometers. Fluorescence emission and excitation spectra were recorded with a Perkin-Elmer LS-5 luminescence spectrometer. The thin films for the registration of UV-Vis absorption and fluorescence spectra were prepared by casting on quartz glass and silica substrates, respectively, from the chloroform solutions. The ionisation potentials (I_p) of the films of the synthesised compounds were measured by the electron photoemission in air method as described before [8,9]. 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 an adhesive layer.

4. Results and discussion

Compound **1** containing electron withdrawing trioxothioxanthene moiety and electron-donating carbazole moiety was synthesised by the synthetic route, shown in Scheme 1. The first step was alkylation of 9H-carbazole with 1,6-dibromohexane using potassium hydroxide in the



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



Scheme 2. Synthesis of compound (**2**).

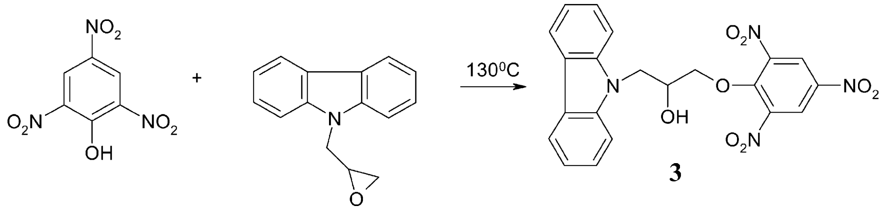
presence of tetrabutylammonium hydrogen sulphate as a phase transfer catalyst. The final step was esterification of 9,10,10-trioxo-9H-3-thioxanthenecarboxylic acid with 6-bromohexyl-9H-carbazole (**a**) in the presence of potassium fluoride in DMF.

9-(6-Benzotriazol-1-yl-hexyl)-9H-carbazole (**2**) was synthesised by alkylation of 1H-benzotriazole with 6-bromohexyl-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.

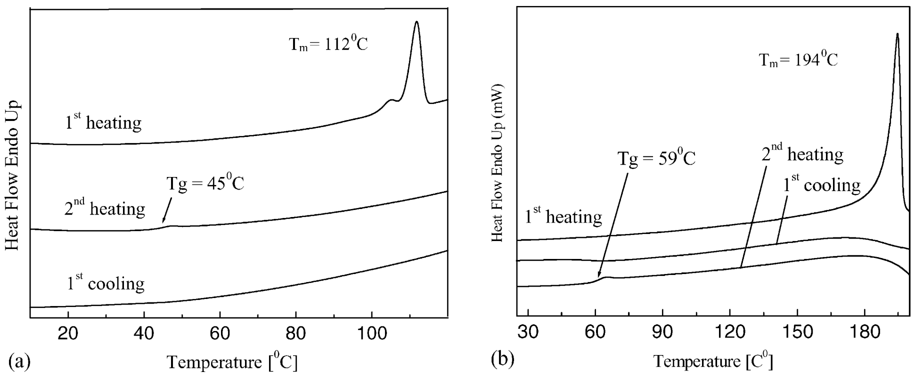
1-(9H-carbazolyl)-3-(2,4,6-trinitrophenoxy)-2-propanol (**3**). It was prepared by the reaction of 2,4,6-trinitrophenol and 9-(2-oxiranylmethyl)-9H-carbazole (Scheme 3). The reaction was carried out in melt. The melting points of the starting materials are 122 and 112 °C, respectively, therefore the reaction was carried out at 130 °C. After heating the reaction mixture for 3 h the yield of 39% of **3** was reached.

The chemical structures of the newly synthesised compounds (**1**–**3**) were confirmed by ^{1}H NMR, IR, spectroscopy and mass spectrometry. These compounds are soluble in common organic solvents such as chloroform, acetone, tetrahydrofuran (THF).

The thermal investigations of the newly synthesised compounds were performed by TGA and DSC. Fig. 1 shows DSC curves of compounds **1** and **3**. The first DSC heating



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



(a) (b)

Fig. 1. DSC curves of **1** (a) and **3** (b) recorded at the heating/cooling rate of 10 °C/min in N_2 atmosphere.

runs of these compounds have revealed melting signals with the maxima at 112 and 194 °C, respectively. Re-cooling revealed no any crystallisation peaks and only glass transitions were observed in the following DSC heating runs at 45 and 59 °C, respectively. 9-(6-Benzotriazol-1-yl-hexyl)-9H-carbazole (**2**) was isolated as the viscous resin and we could only state that its glass transition temperature was below the room temperature.

TGA has revealed relatively high thermal stability of compounds **1** and **3**. Their 5% weight loss temperature is 356 and 229 °C, respectively.

Fig. 2a shows UV-Vis absorption spectra of the dilute solutions of the compounds synthesised. For the comparison UV spectra of the dilute solutions of model compounds bearing the individual chromophores, i.e. carbazole, trioxothioxanthene, trinitrophenol, benzotriazole, are given in Fig. 2b. The absorption spectra of compounds **1** and **2** resemble the sum of the spectra of *N*-ethylcarbazole and the electron-accepting chromophores, i.e. trioxothioxanthene and benzotriazole, respectively. This observation shows that the interaction between the two chromophores is relatively weak in dilute solutions, and it only slightly changes energetic positions of the ground and excited states of the individual chromophores. The new absorption band at 413 nm which is not characteristic neither of the spectrum of *N*-ethylcarbazole nor of the spectrum of trinitrophenol is observed in the UV-Vis spectrum of compound **3**. This observation shows that formation of intermolecular charge transfer complex between the electron-donating (carbazole) and electron-accepting (trinitrophenol) chromophores occurs in the dilute THF solution of **3**. Such complexes are formed through the donor–acceptor linkage, when electron hops from the highest occupied molecular orbital of a donor to the lowest unoccupied molecular orbital of an acceptor [10]. The energy of the system becomes lower when the jump of electron occurs and new band, shifted to the longer wavelengths, appears in an electronic spectrum as the result of the donor–acceptor interaction.

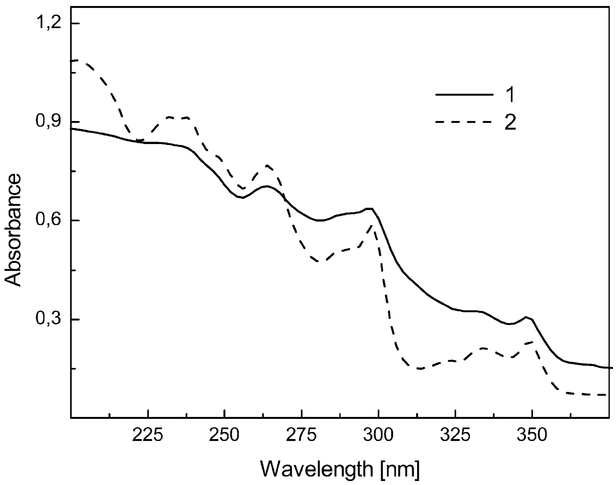


Fig. 3. UV-Vis absorption spectra of the thin films of compounds **1** and **2**.

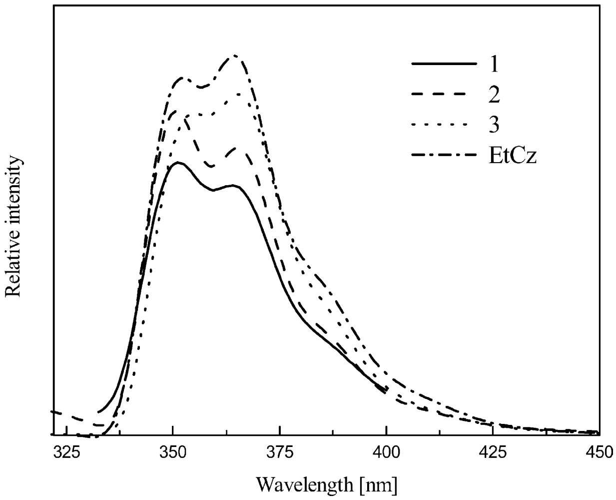


Fig. 4. Fluorescence spectra of dilute THF solutions of compounds **1**–**3** and 3-ethylcarbazole ($c = 10^{-6}$ M, $\lambda_{ex} = 295$ nm).

Fig. 3 shows the absorption spectra of thin amorphous films of compounds **1** and **2**. It was not possible to record UV spectrum of the amorphous film of compound **3** due to its low morphological stability. The comparison of the UV absorption spectra of the amorphous films and dilute solutions shows that the lower energy absorption maxima

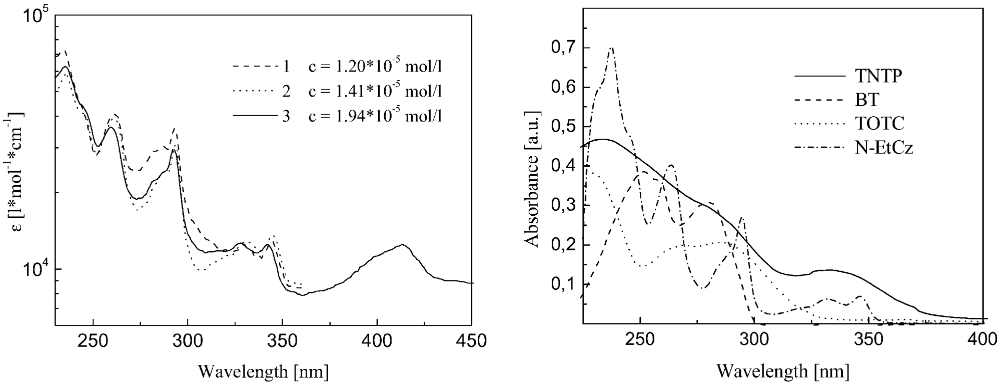


Fig. 2. UV-Vis absorption spectra of the dilute solutions of compounds **1**–**3** (a) and of the model compounds (b): *N*-ethylcarbazole (*N*-EtCz), 1H-benzotriazole (BT), 2,4,6-trinitrophenol (TNTP), 9,10,10-trioxo-9H-3-thioxanthenecarboxylic acid (TOTC) in THF (10^{-5} mol/l).

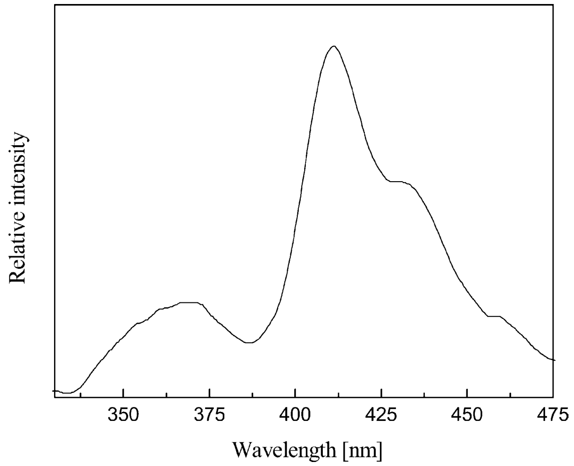


Fig. 5. Fluorescence spectrum of thin film of compound **2** ($\lambda_{ex} = 295$ nm).

undergo small red shifts (4–5 nm) in spectrum of thin films. The absorption red shifts of evaporated thin films, is apparently due to intermolecular interaction. No new absorption bands were observed in the spectra of thin films as compared with the spectra of dilute solutions.

Fig. 4 shows fluorescence spectra of the dilute solutions of compounds **1**–**3**. For the comparison fluorescence spectrum of the dilute solution of *N*-ethylcarbazole is given. All the synthesised compounds exhibit structured fluorescence spectra similar to that of *N*-ethylcarbazole. In the spectrum of dilute solution of compound **3** fluorescence band, the relative intensity of which is by ca. 50 times lower than that of the main fluorescence band, was observed at 514 nm. This is apparently due to intermolecular exciplex emission.

Fluorescence spectrum of thin film of compound **2** is shown in Fig. 5. This thin film exhibits two fluorescence emission maxima at 367 and 411 nm. The shorter wavelength emission band corresponds to a Stokes of shift 1242 cm^{-1} while the longer wavelength emission band has a Stokes shift of 4240 cm^{-1}. The shorter wavelength emission band is observed also in the fluorescence spectrum of dilute solution of **2** and it is conditioned by the monomer emission. The longer wavelength emission band can be assign to an intermolecular exiplex [11]. We did not manage to record Fluorescence from the film of compound **1**. This is apparently due to the intermolecular quenching.

An important characteristic of electronically active compounds used in optoelectronic devices is ionisation potential (I_p), which characterises the electron releasing work under illumination. The I_p values for the films of the synthesised compounds were established by 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 I_p value is determined as the photon energy at the interception point. The photoemission spectra of the amorphous films of compounds **1**–**3** measured at 25 °C, are shown in Fig. 6.

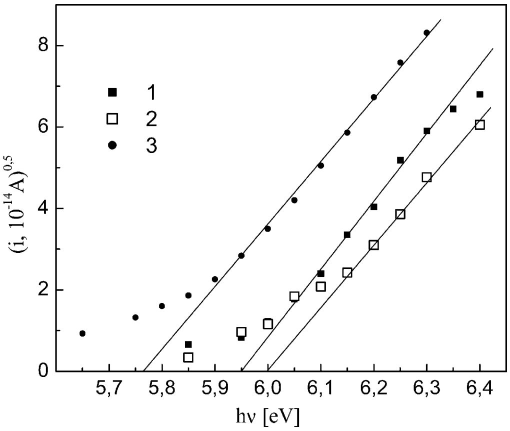


Fig. 6. The photoemission spectra of the amorphous films of compounds **1**–**3**.

Table 1
Ionisation potentials of compounds **1**–**3**

	I_p (eV)
1	5.97
2	~6
3	5.77
PEPK	5.86

The values of ionisation potentials of thin films of the synthesised bipolar compounds are presented in Table 1. For the comparison the value of ionisation potential of carbazole-containing oligoether poly[9-(2,3-epoxypropylcarbazole)] (PEPK) is given [12]. 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. I_p of compounds **1** and **2** are higher than that of PEPK, which means that in the solid state there is an interaction between carbazolyl group and an electron-accepting groups. Only 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.

5. Conclusions

Three bipolar compounds containing acceptor and donor moieties were synthesised and studied. 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 and 59 °C, respectively, as established by differential scanning calorimetry. Absorption spectra 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 thin film of 9-(6-benzotriazol-1-yl-hexyl)-9H-carbazole exhibit two fluoresce maxima at 367 and 411 nm. The blue emission band with the maximum at 411 nm can be assigned to an intermolecular exiplex. The ionisation potentials the synthesised compounds measured by the electron photoemission technique range from 5.77 to ca. 6 eV.

Acknowledgements

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