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Fluorene-based hydrazones and enamines as hole-transporting materials for electrophotography

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Fluorene-based hydrazones and enamines have been synthesized and characterized by various techniques including thermogravimetric analysis, differential scanning calorimetry, UV spectrometry, electron photoemission and time-of-flight techniques. The electron photoemission spectra of the layers of the synthesized materials revealed the ionization potentials of 5.45-6.1 eV. Room temperature hole-drift mobility of 9-(9,9-dihexylfluoren-2-yl)carbazole-3-yl-carbaldehyde N-methyl-N-phenylhydrazone and 2-di(2,2-diphenylvinyl)amino-9,9-dihexylfluorene molecularly dispersed in bisphenol Z polycarbonate exceed 10^{-6} cm^2 V^{-1} s^{-1} at moderate electric fields.

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Keywords: Fluorene; Hydrazone; Enamine; Ionization potential; Hole-drift mobility

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1. Introduction

Organic semiconductors which are also named as charge transport materials are widely used in electrophotographic photoreceptors which are important parts of copying and fax machines as well as laser printers [1]. In practical electrophotographic photoreceptors p-type semiconductors or hole-transporting compounds are mainly used. Arylalkanes, polymeric and low-molar-mass aromatic amines, hydrazones, enamines, oxadiazoles, oxazoles, phthalocyanines, pyrazolines polysilylenes and other materials were reported as hole transport materials for electrophotographic photoreceptors [1]. Different electrophores have been used for the design and synthesis of organic hole-transporting materials. Carbazolyl, triphenylamino, phenothiazinyl groups are apparently the most widely exploited moieties for these purposes. Derivatives of fluorene so far are much less studied as hole transport materials for electrophotography. Such materials are described mainly in the patent literature [2,3]. In the previous paper we reported on the synthesis and properties of carbazolyl- and diphenylamino substituted fluorenes as hole transport materials [4]. Hole-drift mobilities of 50% solid solution of 2,7-dicarbazolyl-9,9-dihexylfluorene in bisphenol Z polycarbonate established by the xerographic time-of-flight technique exceeded 10^{-4} cm^2 V^{-1} s^{-1} at electric field of 10^6 V cm^{-1} In this presentation we report on the synthesis and properties of fluorene-based hydrazones and enamines. Designing these molecules we intended to obtain compounds stable in solid amorphous state. Charge-transporting guests which do not readily crystallize improve morphological stability of molecularly doped polymers and even enable to increase their concentration in the systems [5].

2. Experimental

2.1. Materials

The starting compounds, i.e. 2-bromofluorene, 1-iodohexane, 9*H*-carbazole, *N,N*-diphenylhydrazine hydrochloride, *N*-methyl-*N*-phenyl hydrazine, 2-aminofluorene, 2,2-diphenylacetaldehyde were purchased from “Aldrich” and used as received. All the required chemicals i.e. potassium tert-butoxide, tetrabutylammonium hydrogen sulphate (TBAS), sodium sulphate, 18-crown-6, potassium carbonate, copper powder, phosphorus oxychloride, 10-camphorsulfonic acid were also purchased from “Aldrich”. Organic solvents were purified and dried by standard methods [6]. Silica gel was used for column chromatography.

2-Bromo-9,9-dihexylfluorene (**1**). To a mechanically stirred mixture of 2-bromofluorene (6 g, 24.5 mmol) and dimethyl sulphoxide (DMSO, 50 ml) potassium tert-butoxide (8.2 g, 7.3 mmol), TBAS (0.6 g) and 1-iodohexane (13 g, 6.1 mmol) were added. The resulting mixture was stirred at room temperature for 22 hours. The reaction was stopped by adding water. It was neutralized with 10% HCl till pH=6-7. The crude product was extracted with chloroform for several times. The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was removed. The product was purified by silica gel column chromatography using hexane as an eluent. Yield: 5.26 g (52 %) of $C_{25}H_{33}Br$. FW = 413 g/mol. MS (APCl$^+$, 20 V), *m/z* (%) = 414 ([M+H]$^+$, 90). IR (in KBr) ν/cm^{-1}: 3063, 3024 (CH_{ar}), 2955, 2928, 2857 ($CH_{aliphatic}$), 1466, 1456, 1442 ($C{=}C_{ar}$). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.62-0.67 (m, 4H, $-C\underline{H_2}-CH_3$), 0.81-0.85 (t, 6H, $-CH_2-C\underline{H_3}$), 1.10-1.19 (m, 12H, $-CH_2-C\underline{H_2}-CH_2-$), 1.97-2.03 (m, 4H, $-C-C\underline{H_2}-$), 7.24-7.73 (m, 7H, aromatic protons). ^{13}C NMR

(75.4 MHz, $CDCl_3$), δ (ppm): 14,29 (-$\underline{C}H_3$), 22.87 (-$\underline{C}H_2$-), 23.94 (-$\underline{C}H_2$-), 29.94 (-$\underline{C}H_2$-), 31.75 (-$\underline{C}H_2$-), 40.59 (-$\underline{C}H_2$-), 55.65, 120.01, 121.27, 123.12, 127.24, 126.39, 127.72, 130.15, 140.29, 140.42, 150.56, 153.25 (CH_{ar}).

2-Carbazolyl-9,9-dihexylfluorene (**2**). 1.08 g (2.6 mmol) of 2-brom-9,9-dihexylfluorene, 0.52 g (3.12 mmol) of carbazole, powdered potassium carbonate (2.9 g, 20.9 mmol), copper powder (0.66 g, 10.4 mmol) and 18-crown-6 (0.05 g, 0.18 mmol) were refluxed in 10 ml of *o*-dichlorobenzene under nitrogen for 48 h. Then, copper and inorganic salts were filtered off. The solvent was removed by distillation. The product was purified by silica gel column chromatography using hexane as an eluent. Yield: 0.43 g (33 %) of $C_{37}H_{41}N$ (m.p.: 138 ^{o}C). FW = 499 g/mol. MS ($APCl^+$, 20 V), *m/z* (%) = 500 ($[M+H]^+$, 65). IR (in KBr) ν/cm^{-1}: 3042 (CH_{ar}), 2956, 2928, 2853 ($CH_{aliphatic}$), 1494, 1478, 1456 ($C=C_{ar}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.80-0.87 (m, 10H, -$C\underline{H_2}$-$C\underline{H_3}$), 1.17-1.24 (m, 12H, -CH_2-$C\underline{H_2}$-CH_2-), 2.04-2.09 (m, 4H, -C-$C\underline{H_2}$-), 7.36-8.25 (m, 15H, aromatic protons). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 14.31 (-$\underline{C}H_3$), 22.84 (-$\underline{C}H_2$-), 24.15 (-$\underline{C}H_2$-), 29.94 (-$\underline{C}H_2$-), 31.81 (-$\underline{C}H_2$-), 40.59 (-$\underline{C}H_2$-), 55.66, 110.09, 120.11, 120.16, 120.64, 121.05, 122.07, 123.24, 123.63, 125.99, 126.17, 127.28, 127.68, 136.58, 140.58, 140.73, 141.35, 151.28, 152.84 (CH_{ar}).

2-(3-Formylcarbazolyl)-9,9-dihexylfluorene (**3**). $POCl_3$ (0.63 ml, 6.8 mmol) was added dropwise to dry dimethylformamide (0.63 ml, 8.2 mmol) at 0 °C under N_2 atmosphere. Then the solution of 2-carbazolyl-9,9-dihexylfluorene (**2**) (2 g, 4 mmol) in 10 ml *o*-dichlorobenzene was added stepwise to the reaction flask. The reaction mixture was stirred at 85 °C until the starting compound was consumed. Then the reaction mixture was cooled down to the room temperature, poured into ice water and neutralized with sodium acetate till pH=6-8. The crude product was extracted with chloroform for several times. The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was removed. The product was purified by silica gel column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 8:1. Yield: 1.5 g (71 %) of $C_{38}H_{41}NO$. FW = 527 g/mol. MS ($APCl^+$, 20 V), *m/z* (%) = 528 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3048 (CH_{ar}), 2926, 2854, 2762 ($CH_{aliphatic}$), 1683 (CHO), 1590, 1497, 1461 ($C=C_{ar}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.76-0.87 (m, 10H, -$C\underline{H_2}$-$C\underline{H_3}$), 1.17-1.21 (m, 12H, -CH_2-$C\underline{H_2}$-CH_2-), 2.05-2.11 (m, 4H, -C-$C\underline{H_2}$-), 7.45-8.76 (m, 14H, aromatic protons), 10.19 (s, 1H, -$C\underline{H}O$). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 14.32 (-$\underline{C}H_3$), 22.83 (-$\underline{C}H_2$-), 24.17 (-$\underline{C}H_2$-), 29.91 (-$\underline{C}H_2$-), 31.81 (-$\underline{C}H_2$-), 40.56 (-$\underline{C}H_2$-), 55.76, 110.43, 110.74, 120.34, 121.03, 121.29, 121.44, 122.07, 123.31, 123.54, 123.86, 124.21, 126.06, 127.26, 127.41, 127.74, 128.03, 129.68, 135.46, 140.28, 141.62, 142.36, 144.97, 151.28, 153.14 (CH_{ar}), 191.99 (-$\underline{C}HO$).

0.5-1 g of hydrazones **4** and **5** were prepared by condensation of aldehyde **3** and the corresponding hydrazine by the following general procedure.

A solution of *N*-methyl-*N*-phenylhydrazine (or *N*,*N*-diphenylhydrazine hydrochloride) in iso-propanol was added dropwise to a solution of 2-(3-formylcarbazolyl)-9,9-dihexylfluorene (**3**) in iso-propanol by stirring in a molar ratio of 2 mol of hydrazine to 1 mol of formyl group. The reaction mixture was refluxed for one hour. Then it was cooled down to the room temperature. The product was purified by column chromatography (silica gel, eluent acetone-hexane, 1:3). Compound **5** was crystallized from the mixture of solvents used as an eluent. Compound **4** was isolated as amorphous powder after column chromatography.

9-(9,9-Dihexylfluoren-2-yl)carbazole-3-yl-carbaldehyde N-methyl-N-phenylhydrazone (**4**). Yield: 0.5 g (42 %) of $C_{45}H_{49}N_3$. FW = 631 g/mol. MS ($APCl^+$, 20 V), *m/z* (%) = 632 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3042 (CH_{ar}), 2952, 2925, 2853 ($CH_{aliphatic}$), 1625 (C=N), 1597, 1496, 1459 ($C=C_{ar}$), 1291 (C-N). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.81-0.89 (m, 10H, -$C\underline{H_2}$-$C\underline{H_3}$), 1.18-1.22 (m, 12H, -CH_2-$C\underline{H_2}$-CH_2-), 2.05-2.11 (m, 4H, -C-$C\underline{H_2}$-), 3.54 (s, 3H, -N-$C\underline{H_3}$), 7.29-8.49 (m, 19H, aromatic protons and 1H, C_6H_5-$C\underline{H}$=N-). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 14.35 (-$\underline{C}H_3$), 22.88 (-$\underline{C}H_2$-), 24.18 (-$\underline{C}H_2$-), 29.96 (-$\underline{C}H_2$-), 31.84 (-$\underline{C}H_2$-), 33.45 (-$\underline{C}H_2$-), 40.60 (-N-$\underline{C}H_3$), 55.69, 110.28, 110.36, 115.40, 118.72, 120.19, 120.36, 120.44, 120.81, 121.09, 121.97, 123.97, 123.26, 123.75, 123.90, 124.59, 125.91, 126.34, 127.31, 127.72, 129.33, 129.49, 133.49, 136.45, 140.56, 140.79, 141.25, 141.76, 148.45, 151.29, 152.88 (CH_{ar}).

9-(9,9-Dihexylfluoren-2-yl)carbazole-3-yl-carbaldehyde N,N-diphenylhydrazone (**5**). Yield: 0.9 g (86 %) of $C_{50}H_{51}N_3$ (m.p. 168 ^{o}C). FW = 693 g/mol. MS ($APCl^+$, 20 V), *m/z* (%) = 694 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3049 (CH_{ar}), 2953, 2927, 2855 ($CH_{aliphatic}$), 1627 (C=N), 1589, 1494, 1459 ($C=C_{ar}$), 1298 (C-N). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.85-0.90 (m, 10H, -$C\underline{H_2}$-$C\underline{H_3}$), 1.17-1.25 (m, 12H, -CH_2-$C\underline{H_2}$-CH_2-), 2.05-2.11 (m, 4H, -C-$C\underline{H_2}$-), 7.28-8.36 (m, 24H, aromatic protons and 1H, C_6H_5-$C\underline{H}$=N-). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 14.36 (-$\underline{C}H_3$), 22.88 (-$\underline{C}H_2$-), 24.19 (-$\underline{C}H_2$-), 29.96 (-$\underline{C}H_2$-), 31.84 (-$\underline{C}H_2$-), 40.60 (-$\underline{C}H_2$-), 55.69, 110.29, 110.36, 119.25, 120.20, 120.42, 120.78, 121.10, 121.97, 122.89, 123.27, 123.70, 123.82, 124.55, 124.62, 125.91, 126.36, 127.32, 127.75, 128.76, 130.08, 136.37, 137.27, 140.53, 140.85, 141.46, 141.75, 144.31, 151.28, 152.89 (CH_{ar}).

2-Di(2,2-diphenylvinyl)aminofluorene (**6**). 2,2-Diphenylacetaldehyde (6.5 g, 33.2 mmol) was added dropwise to a solution of 2-aminofluorene (3 g, 16.6 mmol) in 15 ml toluene by stirring. Catalytical amount of 10-camphorsulfonic acid was introduced into the reaction mixture. The reaction mixture was heated at 80 ^{o}C for 4 h. Then the solvent was evaporated under vacuum and the residue was purified by silica gel column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 20:1. Yield: 2.1 g (70 %) of $C_{41}H_{31}N$ (m.p. 194 ^{o}C). FW = 537 g/mol. MS ($APCl^+$, 20 V), *m/z* (%) = 538 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3224 (CH_{ar}), 1488, 1454 ($C=C_{ar}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.93 (s, 2H, -$C\underline{H_2}$-), 6.03-7.89 (m, 27H, aromatic protons and 2H, C=$C\underline{H}$-Ph_2). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 37.22 (-$\underline{C}H_2$-), 114.18, 116.42, 125.19, 126.15, 126.78, 127.04, 127.49, 127.98, 128.59, 128.89, 129.37, 129.86, 130.38, 132.35, 132.74, 140.39, 141.68, 143.01, 145.21 (CH_{ar}).

2-Di(2,2-diphenylvinyl)amino-9,9-dihexylfluorene (**7**) was prepared by alkylation of 2-di(2,2-diphenylvinyl)aminofluorene (**6**) according to the procedure given for compound **1**. The product was purified by silica gel column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 20:1. Yield: 1.1 g (41 %) of $C_{53}H_{55}N$ (m.p.: 134 ^{o}C). FW = 705 g/mol. MS (APCl^{+}, 20 V), *m/z* (%) = 706 ($[M+H]^{+}$, 100). IR (in KBr) ν/cm^{-1}: 3049, 3021 (CH_{ar}), 2958, 2925, 2846 ($CH_{aliphatic}$), 1595, 1568, 1451 ($C{=}C_{ar}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.74-0.78 (m, 4H, $-C\underline{H_2}-CH_3$), 0.83-0.88 (t, 6H, $-CH_2-C\underline{H_3}$), 1.11-1.16 (m, 12H, $-CH_2-C\underline{H_2}-CH_2-$), 1.98-2.04 (m, 4H, $-C-C\underline{H_2}-$), 6.02-7.71 (m, 27H, aromatic protons and 2H, $C{=}C\underline{H}-Ph_2$). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 14.37 ($-\underline{C}H_3$), 22.83 ($-\underline{C}H_2-$), 23.96 ($-\underline{C}H_2-$), 29.84 ($-\underline{C}H_2-$), 31.74 ($-\underline{C}H_2-$), 40.53 ($-\underline{C}H_2-$), 55.53, 111.75, 116.46, 119.21, 120.47, 123.01, 126.34, 126.99, 127.46, 128.01, 128.88, 129.85, 132.25, 135.93, 140.52, 141.29, 141.71, 145.52, 150.54, 152.89 (CH_{ar}).

2.2. Instrumentation

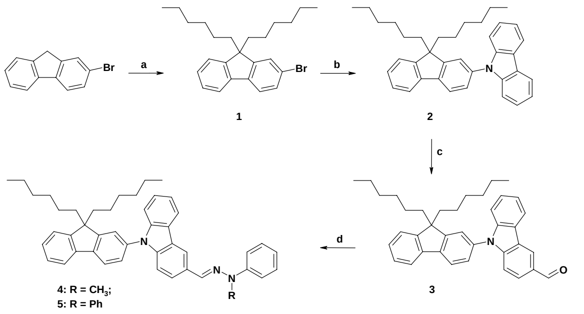
^{1}H NMR and ^{13}C NMR spectra of the solutions of the synthesized compounds in deuterated chloroform were taken on a Varian Unity Inova (300 MHz (^{1}H), 75.4 MHz (^{13}C)) spectrometer. All the data are given as chemical shifts δ (ppm) downfield from $Si(CH_3)_4$. IR spectra were recordered using Perkin Elmer FT-IR System. The spectra of the solid compounds were performed in a form of KBr pellets. Electron impact mass spectra were obtained on a Waters 2Q 2000. The UV spectra of 10^{-5} M solutions of the synthesized compounds in THF were recorded on a CARY 219 spectrometer using a microcell with an internal width of 1 mm. Fluorescence emission and excitation spectra were recorded with a Hitachi MPF-4 (Japan) luminescence spectrometer.

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin-Elmer DSC-7 at 10 ^{o}C min^{-1} heating rate under nitrogen atmosphere. The glass transition temperatures (T_g) were determined from the second heating scans. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851^{e} at a 10 ^{o}C min^{-1} heating rate under nitrogen atmosphere. Melting points were measured on a Buchi 510 melting point apparatus.

The ionization potentials (I_p) of the films of the synthesized compounds were measured by electron photoemission in air method as described before [7]. Hole-drift mobilities of the synthesized materials molecularly doped in bisphenol Z polycarbonate (PC-Z) were estimated by a xerographic time-of-flight (XTOF) method [8,9].

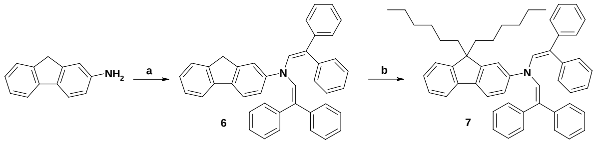
3. Results and discussion

Fluorene-based hydrazones **4** and **5** were synthesized as described in Scheme 1 by multistep synthetic route involving the alkylation of bromofluorene, Ullmann coupling reaction of 2-bromo-9,9-dihexylfluorene with 9*H*-carbazole, Vilsmeyer formylation and the condensation of the aldehyde obtained with differently substituted hydrazines.



Scheme 1. (a) 1-iodohexane, potassium tert-butoxide, TBAS, DMSO, r.t., 22 h; (b) Cu, K_2CO_3, 18-crown-6, o-dichlorobenzene, 9H-carbazole, 180 ^{o}C, 48 h; (c) $POCl_3$/DMF complex, o-dichlorobenzene, 85 ^{o}C, 24 h; (d) iso-propanol, N,N-diphenylhydrazine hydrochloride for 4 and N-methyl-N-phenyl hydrazine for 5, reflux, 1 h.

Fluorenyl-containing enamines **6** and **7**, the structures of which are shown in Scheme 2, were synthesized by the reaction of 2-aminofluorene with 2,2-diphenylacetaldehyde followed by the alkylation.



Scheme 2. (a) 10-camphorsulfonic acid, toluene, 2,2-diphenylacetaldehyde, 80 ^{o}C, 4h; (b) 1-iodohexane, potassium tert-butoxide, TBAS, DMSO, r.t., 22 h.

The synthesized compounds were characterized by IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry as described in the Experimental section. They are soluble in common organic solvents such as chloroform, acetone, tetrahydrofuran.

The thermal properties of the fluorene-based hydrazones and enamines were examined by DSC and TGA under a nitrogen atmosphere. Fluorene-based hydrazone having methylphenyl substituents at the hydrazine N atom **4** and enamine **6** were isolated as amorphous substances as confirmed by DSC. When the sample of hydrazone **4** was heated the glass-transition was observed at 45 ^{o}C and no peaks due to crystallization and melting appeared. Cooling down and the following repeated heating revealed only the glass transition again.

The diphenyl-substituted hydrazone **5** and alkylated enamine **7**, which were isolated as crystalline materials, show melting only in the first DSC heating scan and form glasses upon cooling from the melt. The second heating scan revealed only glass transition at 51 °C for **5** and 49 °C for **7** and no signals due to crystallization and melting. As an illustration of the DSC thermograms of fluorene-containing hydrazone **5** are presented in Fig. 1.

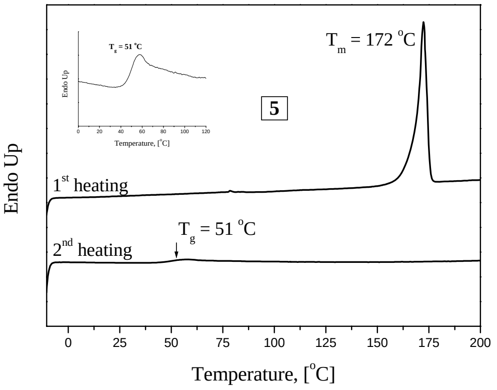


Fig. 1. DSC curves of fluorene-based hydrazone 5, at the heating rate of 10 °C min^{-1}, N_2 atmosphere.

The values of glass transition temperatures (T_g), melting points (T_m) and 5% weight loss temperatures (T_{ID}) of compounds **4, 5** and **7** are summarized in Table 1.

Table 1. Thermal characteristics of the fluorene-based compounds 4, 5 and 7.

Compound	T_g [°C]	T_m [°C]	T_{ID}^{a} [°C]
4	45	-	290
5	51	172^b	264
7	49	137^b	333

[a] T_{ID} is the temperature at which 5% loss of mass was observed in a thermogravimetric experiment with a heating rate of 10 K min^{-1};

[b] 1st heating only.

The comparison of the values of T_g of diphenyl-substituted hydrazone **5** and methylphenyl-substituted hydrazone **4** shows that the T_g of compound **5** is by 6 degrees higher than that of compound **4**. The similar observation was earlier reported for carbazole-based hydrazones [10]. DSC did not reveal neither melting nor crystallization signals for the sample of **6**, neither during the first nor the following heating and cooling scans. Unfortunately we were also unable to fix the glass transition temperature for **6**. Only smooth DSC curves were observed both for heating and cooling scans. Thus we could only state that compound **6** is an amorphous material.

Hydrazones **4**, **5** and enamine **7** demonstrate relatively high thermal stability. 5% mass loss temperature of enamine **7** is markedly enhanced as compared to that of hydrazones. This is the expected result since earlier we observed even higher thermal stability for carbazole-based enamines [11]. 5% mass loss for hydrazone **5**, having diphenyl substituted hydrazine nitrogen atoms, is observed at 264 °C, while compound **4**, containing methylphenyl substituted nitrogen atom, shows a corresponding mass loss at 290 °C. Very similar thermal stabilities were earlier observed for carbazole-containing hydrazones [**Error! Bookmark not defined.**].

The synthesized compounds absorb electromagnetic radiation in the 240-450 nm region. The absorption spectra of hydrazones **4** and **5**, which are shown in Fig. 2a, are similar due to their similar structure. For a comparison the spectrum of the starting compound **2** is given in Fig. 2a. The low energy absorption bands of hydrazones **4**, **5** exhibit strong bathochromic and hyperchromic shifts with respect to the spectrum of compound **2**. This is the outcome of extended π-electron conjugation system in compounds **4** and **5**. UV absorption bands of diphenyl-substituted hydrazone **5** exhibit higher values of molar extinction coefficient and small bathochromic shifts with respect of the corresponding bands of methylphenyl-substituted hydrazone **4**. UV-vis absorption spectra of the dilute solution of enamines **6** and **7** are given in Fig. 2b. For the comparison the spectrum of dilute solution of fluorene is given. The spectra of enamines **6** and **7** exhibit new low energy absorption bands at 361 nm for enamine **6** and 364 nm for compound **7**, which are not characteristic of the spectrum of fluorene. This is also, apparently, the consequence of the increased conjugated π-electron system of **6** and **7**.

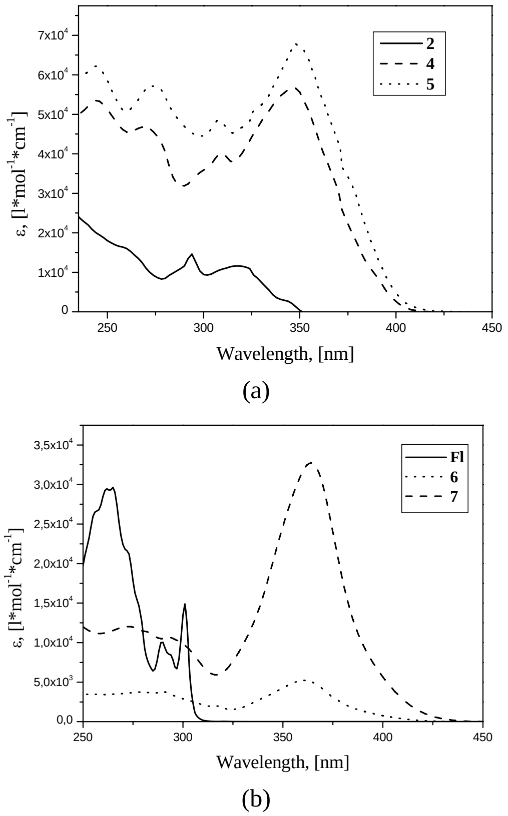


Fig. 2. UV-vis absorption spectra of dilute THF solutions (10^{-5} mol l^{-1}) of fluorenyl-containing compounds 2, 4, 5 (a) and of compound 6, 7 and fluorene (b).

Fig. 3 shows fluorescence spectra of dilute solutions of the synthesized compounds. For the comparison the spectra of dilute solutions of fluorene and 2-carbazolyl-9,9-dihexylfluorene (**2**) are given. The fluorescence band of diphenyl substituted hydrazone **5** with the maximum at 406 nm is red shifted with respect of the fluorescence band of methylphenyl substituted hydrazone **4**, with the maximum at 380 nm. The bands of fluorescence spectra of all the synthesized compounds are shifted towards the long wavelength region with respect of the bands of fluorene and 2-carbazolyl-9,9-dihexylfluorene (**2**).

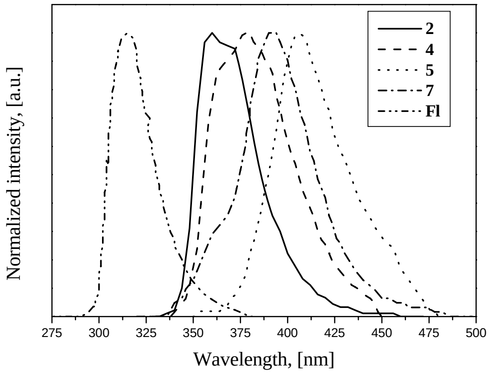


Fig. 3. Fluorescence spectra of dilute THF solutions of fluorenyl-containing compounds 2, 4, 5, 7 and fluorene ($c = 10^{-5}$ mol l^{-1}). For 2, 4, 5 and 7 $\lambda_{ex} = 330$ nm, for fluorene $\lambda_{ex} = 260$ nm.

Amorphous thin films on substrates can be prepared by casting or spin coating techniques from all the synthesized materials. Fig. 4 shows electron photoemission spectra of the amorphous films of all compounds **4-7**. The intersection points of the straight lines drown with the abscissa axis gives the values of the ionization potential, which are summarized in Table 2.

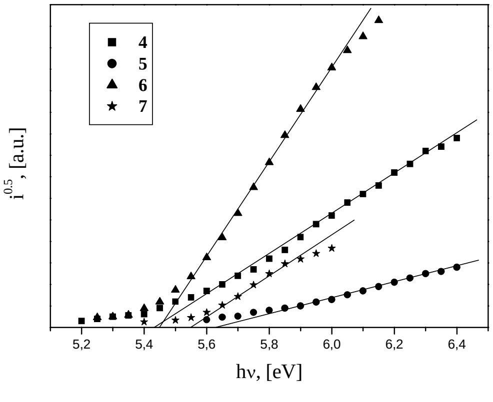


Fig. 4. The electron photoemission spectra in air of the films of compounds 4-7.

Table 2. Ionization potentials of the amorphous films of fluorenyl-containing compounds 2 and 4-7.

Compound	2	4	5	6	7
I_p, [eV]	6.10	5.50	5.60	5.45	5.55

I_p values of fluorene-based hydrazones **4**, **5** and enamines **6**,**7** are rather close. They lower than that of compound **2**, which was used in the synthesis of these materials. This observation is consistent with absorption and fluorescence spectrosopy data. The spectra of hydrazones **4**, **5** and enamines **6**,**7** are red shifted with respect of the spectra of compound **2**.

The room temperature electric field dependencies of hole drift mobility (μ) values for the solid solutions of the synthesized compounds in PC-Z are given in Fig. 5. Unfortunately because of the relatively low solubility of most of the synthesized compounds we were not able to prepare the solid solutions of the equal and high enough concentration for the time-of-flight measurements. Only enamine **7** showed good enough solubility for the preparation of 50 wt.% solid solutions in PC-Z. The other systems studied had lower concentration of charge-transporting compound. For this reason the direct comparison of charge transport properties of the synthesized materials is impossible. The linear dependencies of the hole-drift mobility on the square root of the electric field E are observed which means that in all the cases drift mobility may be well approximated by the formula $\mu = \mu_0 \exp(\alpha\sqrt{E})$, where α is Pool-Frenkel parameter, μ_0 is zero field mobility. Such dependencies of charge mobility on electrical field are characteristic of many organic semiconductors and are predicted by the Bässler-Borsenberger model [12]. It is evident from the data presented in Fig. 5, that hole mobilities in PC-Z doped with enamines **6** and **7** are much less electric field dependent than those in PC-Z doped with hydrazones **4** and **5**. The highest hole drift mobilities were observed for 40% solid solution of hydrazone **4** and 50% solution of enamine **7** in PC-Z. They exceed 10^{-6} cm^2 V^{-1} s^{-1} at an electric field of 10^6 V cm^{-1}.

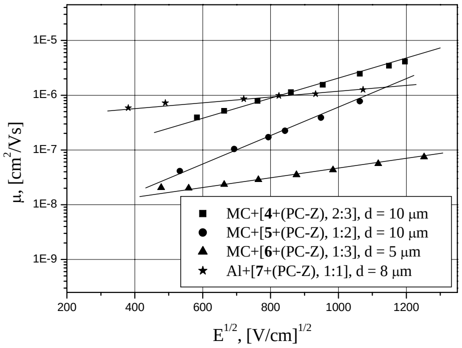


Fig. 5. Electric field dependencies of hole drift mobilities (μ) of fluorene-based hydrazones 4, 5 and enamines 6, 7 doped in PC-Z (mass proportion 2:3, 1:2, 1:3 and 1:1 respectively).

In conclusion, we have synthesized new fluorene-based hydrazones and enamines and have studied their optical, thermal and optoelectrical properties. The synthesized compounds show high thermal stability and form glasses with glass transition temperatures ranging from 45 °C to 51 °C. The ionization potentials were measured by the electron photoemission in air method and were found to range from 5.45 eV to 6.1 eV. Hole-drift mobilities of the solid solutions of fluorene-based hydrazone and enamine in bisphenol Z polycarbonate established by the xerographic time-of-flight technique exceed 10^{-6} $cm^2 V^{-1} s^{-1}$ at moderate electric fields.

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