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N,N'-Bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidines with reactive functional groups as hole-transporting glass-forming materials

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Derivatives of N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine containing reactive functional groups were synthesized by the multi-step synthetic rout. The materials were examined by various techniques including differential scanning calorimetry, UV and fluorescence spectrometry, electron photoemission and time of flight techniques. The electron photoemission spectra of layers of the amorphous materials showed the ionization potentials of 5.35 eV. Hole drift mobilities in the layers of bisphenol Z polycarbonate containing 33-50% of the derivatives of N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine range from 1.6×10^{-5} to 1.3×10^{-4} cm^2/Vs at high electric fields.

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1. Introduction

Low-molar-mass organic compounds that readily form stable glasses receive growing attention both in terms of academic interest and technological applications [1-3]. Some of these derivatives belong to the classes of electro-active materials, and are known for various applications such as organic light-emitting diodes, photovoltaic cells and electro-photographic photoreceptors [4-7].

Important components of these devices are hole transporting materials, which are usually either of π-conjugated polymers or of electron- donating triarylamine derivatives. Among the derivatives of triarylamine , N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) and its derivatives are the most extensively used as charge-transporting materials [8]. TPD is easily oxidized to form stable radical cation [9,10]. However, the amorphous layers of the low-molecular-weight compound have some drawbacks such as the lack of the morphological and thermal stability [11].

Earlier we have described [3,3′]bicarbazole based enamines, [12]. In this work, we have designed and synthesised new triphenyldiamine derivatives having enamine fragments, which were expected to enhance hole injection and transport properties of the materials. In addition, some of these compounds contain reactive oxyranyl moieties. Organic electroactive compounds which can be (photo)polymerized/cross-linked directly in thin films, can be applied in manifold ways for organic optoelectronics [13,15]. Recently photo-cross-linking is a common strategy of protecting thin organic systems against solvents [16,18,19]

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using Varian Unity Inova (300 MHz) apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FTIR spectra were recorded using Perkin Elmer FT-IR System. UV spectra were measured with a Spectronic Genesys^{TM} 8 spectrometer. Fluorescence (FL) spectra were recorded with a MPF- 4 spectrometer.

Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10^o C/min.

The ionization potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [20]. The measurement method was, in principle, similar to that demonstrated by Miyamoto et al. [21].The samples for the ionisation potential measurement were prepared as follows. The materials were dissolved in THF and were coated on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of this layer is not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, the MKM layer is conductive enough to avoid charge accumulation on it during the measurements. The thickness of the layers was 0.5-1 μm.

Hole drift mobility was measured by the xerographic time of flight technique [22,23]. The samples for the charge carrier mobility measurements were prepared by procedure as we described earlier [24].

2.2. Materials

N,N'-diphenylbenzidine (**1**), 2,2-diphenylacetaldehyde, $POCl_3$, $NaBH_4$, epichlorohydrin, tetra-n-butylammonium hydrogen sulfate (TBAS) and (±)-camphor-10-sulfonic acid were purchased from Aldrich and used as received.

N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine (**2**) was prepared from N,N'-diphenylbenzidine (**1**) and 2,2-diphenylacetaldehyde in the presence of catalytic amount of (±)-camphor-10-sulfonic acid by similar procedures as described in literature [25-27].

N,N'-bis(2,2-diphenylvinyl)-N-phenyl-N'-(4-formylphenyl)benzidine (**3**) and N,N'-bis(2,2-diphenylvinyl)-N,N'-di(4-formylphenyl)benzidine (**4**) were synthesized from N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine (**2**) by Vilsmeier procedure [28]. $POCl_3$ (0.44 g, 3 mmol) was added drop-wise to 1 ml of dry DMF at 0°C under nitrogen atmosphere. Compound **2** (2 g, 3 mmol), which was dissolved in 50 ml of chloroform, was added to the mixture. The resulting mixture was stirred at 80°C until the starting compound **3** reacted completely. Then the mixture was cooled down to the room temperature, poured into ice water and neutralized with sodium acetate till pH= 6- 8. The precipitated material was filtered and separated to compounds **3** and **4** by silica gel column using hexane/ethyl acetate (vol. ratio 20:1) as an eluent. Yield: 0.9 g of **3** and 0.6 g of **4**.

N,N'-bis(2,2-diphenylvinyl)-N-phenyl-N'-(4-formylphenyl)benzidine (**3**).

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 9.78 (s, 1H, CHO); 7.62 (d, 2H, J = 8.4 Hz, Ar); 7.31 – 7.21 (m, 14H, Ar); 7.23 – 6.86 (m, 21H, Ar); 6.76 (s, 2H, N-CH=).

MS(APCI$^+$, 20 V, m/z): 721.4 ([M+H]$^+$, 100 %).

IR (KBr, cm^{-1}): 3053, 3026 (C-H, Ar); 2951, 2923 (C-H); 2852, 2724 (CHO); 1690 (C=O); 1589, 1566 (C=C); 1491, 1442 (C-C, Ar); 1319, 1302, 1258 (C-N); 819, 759, 695 (C-H, Ar).

N,N'-bis(2,2-diphenylvinyl)-N,N'-di(4-formylphenyl)benzidine (**4**).

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 9.79 (s, 2H, CHO); 7.64 (d, 4H, J = 9.1 Hz, Ar); 7.31 – 7.28 (m, 10H, Ar); 7.25 (d, 4H, J = 8.6 Hz, Ar); 7.1 -6.9 (m, 18H, Ar); 6.77 (s, 2H, N-CH=).

MS(APCI$^+$, 20 V, m/z): 749.9 ([M+H]$^+$, 100 %).

IR (KBr, cm^{-1}): IR (KBr), (cm^{-1}): 3028 (C-H, Ar); 2799, 2717, 2689 (CHO); 1688 (C=O); 1588, 1552 (C=C); 1505, 1492 (C-C, Ar); 1333, 1306, 1256 (C-N); 821, 746, 696 (C-H, Ar).

N,N'-bis(2,2-diphenylvinyl)-N-phenyl-N'-(4-hydroxymethylphenyl)benzidine (**5**). N,N'-bis(2,2-diphenylvinyl)-N-phenyl-N'-(4-formylphenyl)benzidine (**3,** 0.55 g, 0.8 mmol) was dissolved in the mixture of methanol (10 ml) and THF (10 ml). $NaBH_4$ (0.05 g, 1.3 mmol) was added to the solution by small portions. The resulting mixture was refluxed for 0.5 h. When the reaction was finished, the reaction mixture was poured into ice water. The product was extracted by chloroform. The organic fraction was dried by $MgSO_4$ and the solvent was removed by evaporation. The product was crystallized from the mixture of hexane and diethyl ether. Yield: 0.5 g of yellow material **5**.

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 7.28 – 6.25 (m, 36 H, Ar); 6,76 (s, 1H, N-CH=); 6.74 (s, 1H, N-CH=); 4.53 (s, 2H, Ar-CH_2-O-); 1.56 (s, 1H, -OH).

MS(APCI$^+$, 20 V, m/z): 723.4 ([M+H]$^+$, 80 %).

IR (KBr, cm^{-1}): IR (KBr), (cm^{-1}): 3285 (O-H); 3052, 3025 (C-H, Ar); 2950, 2922, 2852 (C-H); 1590, 1569 (C=C); 1491, 1442 (C-C, Ar); 1329, 1316, 1256 (C-N); 1026,1001 (C-O); 819, 759, 695 (C-H, Ar).

N,N'-bis(2,2-diphenylvinyl)-N,N'-di(4-hydroxymethylphenyl)benzidine (**6**) was synthesyzed from 0.46 g (0.6 mmol) of N,N'-bis(2,2-diphenylvinyl)-N,N'-di(4-formylphenyl)benzidine (**4**) and 0.05 g (1.3 mmol) of $NaBH_4$ by the similar procedure as described for derivative **5**. The crude product was directly used for next step syntheses. Yield: 0.37 g of yellow material.

N,N'-bis(2,2-diphenylvinyl)-N-phenyl-N'-(4-oxyranylmethoxymethylphenyl)benzidine (**7**). 0.3 g (0.4 mmol) of N,N'-bis(2,2-diphenylvinyl)-N-phenyl-N'-(4-hydroxymethyl-phenyl)benzidine (**5**) was dissolved in 0.5 g (6 mmol) of epichlorohydrin. KOH (0.07 g, 1.2 mmol), K_2CO_3 (0.06 g, 0.5 mmol) and catalytic amount of TBAS were added to the solution. The resulting mixture was stirred at 50°C for 1 h, i.e. until the starting compound **5** all was reacted. Then the reaction mixture was filtered, excess of epichlorohydrin was removed by distillation and the crude product was purified by silica gel column using hexane/ethyl acetate (vol. ratio 5:1) as an eluent. After the purification the derivative **7** was crystallized from the eluent to yield 0.13 g of crystalline material (mp 87 ºC).

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 7.24 – 7.2 (m, 7H, Ar); 7.12 – 6.88 (m, 30H, Ar); 6.76 (s, 1H, N-CH=); 6.74 (s, 1H, N-CH=); 4.44 (dd, 2H, J_1 = 11.7 Hz, J_2 = 19 Hz, Ar-CH_2-O-); 3.64 (dd, 1H, J_1 = 3.1 Hz, J_2 = 11.4 Hz, Ar-CH_2-O-$\underline{CH_2}$-); 3.35 (dd, 1H, J_1 = 5.7 Hz, J_2 = 11.4 Hz, Ar-CH_2-O-$\underline{CH_2}$-); 3.19 – 3.13 (m, 1H, -O-CH_2-$\underline{CH}$); 2.8 (dd, 1H, J_1 = 5.2 Hz, J_2 = 4.1, -CH_2- of epoxy group); 2.61 (dd, 1H, J_1 = 5.2 Hz, J_2 = 2.7 Hz, -CH_2 of epoxy group).

MS(APCI$^+$, 20 V, m/z): 779.3 ([M+H]$^+$, 70 %).

IR (KBr, cm^{-1}): IR (KBr), (cm^{-1}): 3050, 3029 (C-H, Ar); 2972, 2921, 2853 (C-H); 1602, 1590 (C=C); 1491, 1443 (C-C, Ar); 1342, 1315, 1273, 1257 (C-N); 1103, 904, 876 (C-O-C); 832, 818, 760, 696 (C-H, Ar).

N,N'-bis(2,2-diphenylvinyl)-N,N'-di(4-oxyranylmethoxymethylphenyl)benzidine (**8**). 0.46 g (0.6 mmol) of N,N'-bis(2,2-diphenylvinyl)-N,N'-di(4-hydroxymethylphenyl)benzidine (**6**) was dissolved in 2 g (22 mmol) of epichlorohydrin. KOH (0.5 g, 8.9 mmol), K_2CO_3 (0.39 g, 3 mmol) and catalytic amount of TBAS were added to the solution. The resulting mixture was stirred at 50°C for 2 h, i.e. until the starting compound **6** reacted completely. Then the reaction mixture was filtered, the excess of epichlorohydrin was removed by distillation and the crude product was purified by silica gel column chromatography using hexane/ethyl acetate (vol. ratio 2:1) as an eluent. After the purification compound **8** was crystallized from the eluent to yield 0.36 g of crystalline comound (mp 181 ºC).

^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 7.3 – 7.21 (m, 14H, Ar); 7.1 – 6.92 (m, 22H, Ar); 6.74 (s, 2H, N-CH=); 4.45 (dd, 4H, J_1 = 12 Hz, J_2 = 19.5 Hz, Ar-CH_2-O-); 3.65 (dd, 2H, J_1 = 3.2 Hz, J_2 = 11.3 Hz, Ar-CH_2-O-$\underline{CH_2}$-); 3.35 (dd, 2H, J_1 = 5.6 Hz, J_2 = 11.3 Hz, Ar-CH_2-O-$\underline{CH_2}$-); 3.1 – 3.14 (m, 2H, -O-CH_2-$\underline{CH}$); 2.81 (dd, 2H, J_1 = 5.1 Hz, J_2 = 4.3 Hz, -CH_2- of epoxy group); 2.61 (dd, 2H, J_1 = 5.1 Hz; J_2 = 2.8 Hz, -CH_2- of epoxy group).

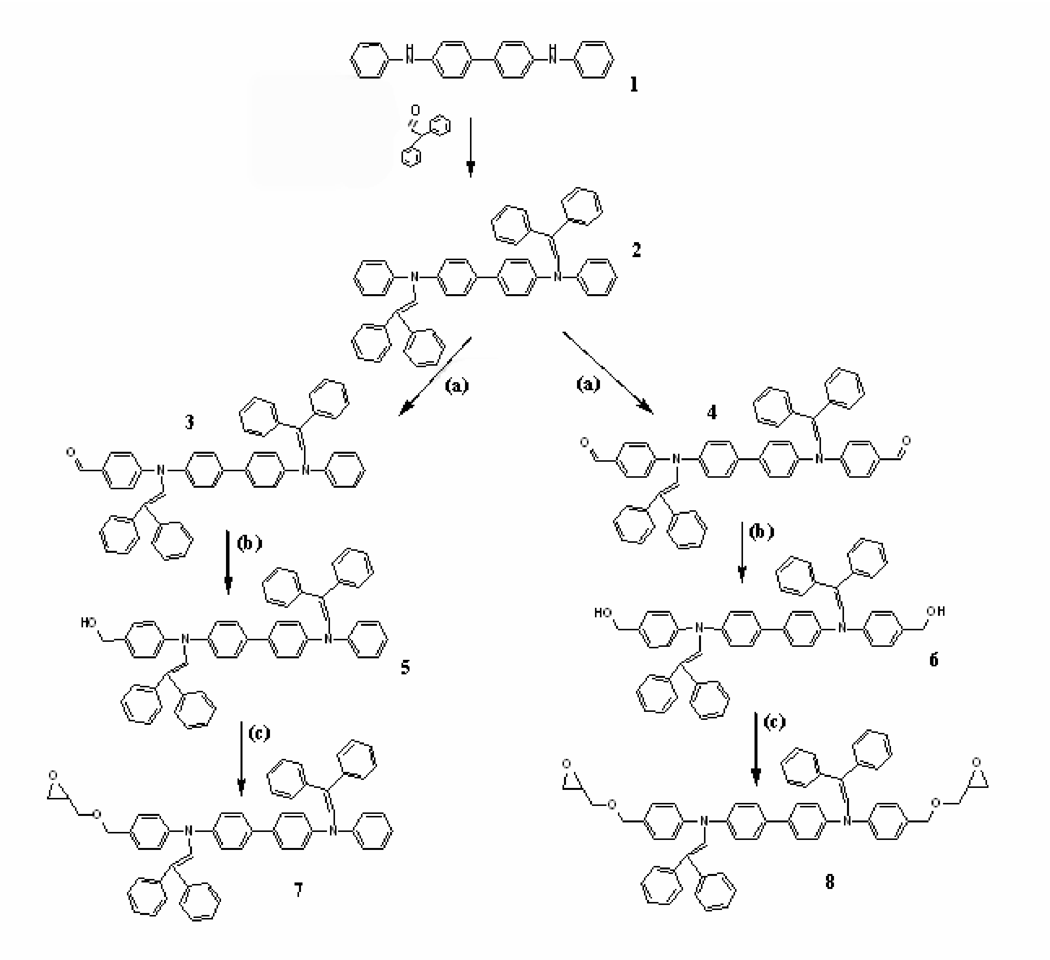
MS(APCI$^+$, 20 V, m/z): 865.4 ([M+H]$^+$, 95 %).

IR (KBr, cm^{-1}): IR (KBr), (cm^{-1}): 3048, 3030, 2996 (C-H, Ar); 2920, 2849 (C-H); 1602, 1590 (C=C); 1511, 1492 (C-C, Ar); 1346, 1274 (C-N); 1102 (C-O-C); 1250, 904, 877(C-O-C in epoxy group); 833, 766, 697 (C-H, Ar).

The synthetic rout towards the N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine-based derivatives is shown in Scheme 1. The key starting compound N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine (**2**) was prepared from commercially available N,N'-diphenylbenzidine (**1**) and 2,2-diphenylacetaldehyde in the presence of catalytic amount of (±)-camphor-10-sulfonic acid by the similar procedure as described in literature [25-27]. Compound **2** was converted to mono- and diformyl derivatives **3** and **4**, respectively, using Vilsmeier formylation procedure [28]. Hydroxymethyl-substitited derivatives **5** and **6** were obtained by reduction of the aldehydes (**3** and **4**) with sodium borohydride in methanol. Compound **5** was converted into the epoxy derivative **7** by its reaction with an excess of epichlorohydrin under basic conditions. Two functional oxyranyl groups containing cross-linkable compound **8** was prepared from dihydroxy derivative **6** and epichlorohydrin by the similar procedure.

The newly synthesized compounds were identified by mass spectrometry, IR and ^{1}H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. Compounds **7** and **8** are soluble in common organic solvents at room temperature.

3. Results and discussion



Scheme 1. (a) $POCl_3$/dimethylfomamide; (b) $NaBH_4$; (c) epichlorohydrin.

The behaviour under heating of compounds **7** and **8** was studied by DSC and TGA under nitrogen atmosphere. The materials demonstrate rather high thermal stability. Their initial loss of mass was observed at temperatures higher than 330 °C as confirmed by TGA with a heating rate of 10 °C/min.

The derivatives **7** and **8** were obtained as crystalline materials after the synthesis. However they readily formed glasses when the melt samples were cooled down. The DSC thermograms of **7** are shown in Fig. 1. When the crystalline sample was heated, the endothermic peak due to melting was observed at 87 °C. When the melt sample was cooled down and heated again, the glass-transition was observed ca 30 °C and on further heating no peaks due to crystallization and melting appeared. The crystalline sample of compound **8** demonstrated the similar behaviour. It melted on first heating at 181 °C and formed glass (T_g = 62 °C) upon cooling.

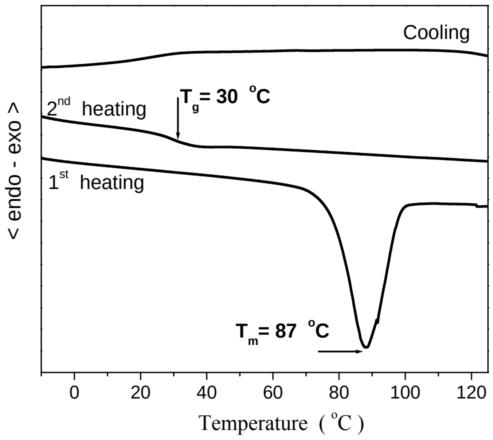
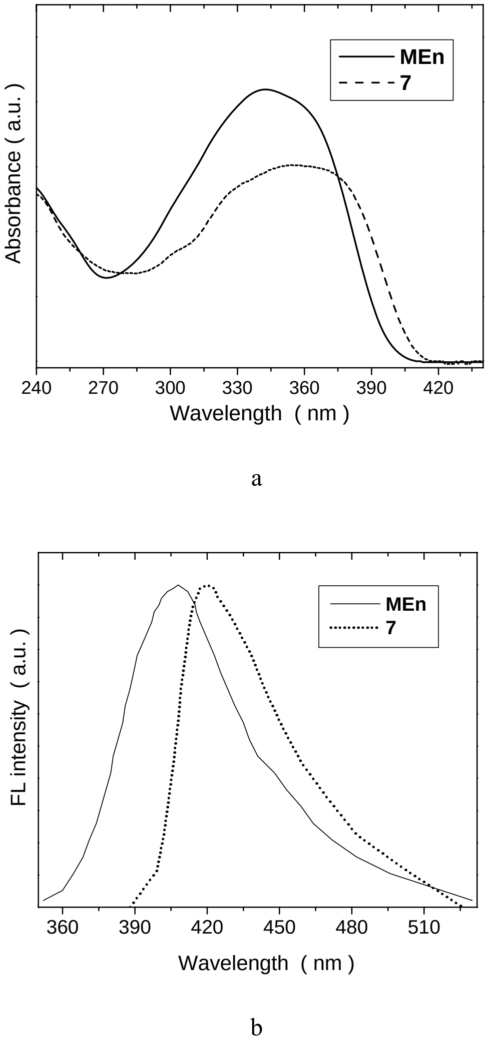


Fig. 1. DSC curves of compound 7. Heating rate 10 °C/min.

UV absorption and FL spectra of dilute solutions of the compounds synthesized were recorded. The spectra of compound **7** are presented in Fig. 2 The solutions of **8** demonstrated analogous absorption and emission properties. The electronic absorption energies of compounds **7-8** are comparable, and the wavelengths of absorption maxima (λ_{max}) are observed at ca 360 nm. The wavelengths of FL maxima of the derivatives are very close and appear at ca. 420 nm. UV absorption and FL spectra of dilute solutions of corresponding derivative containing only one enamine fragment, i.e. N-(2,2-diphenylvinyl)-N'-(2-ethylhexyl)-N,N'-diphenylbenzidine (**MEn**), are presented in the Fig. 2 for the comparison. The synthesis of the derivative **MEn** was described earlier [29]. It is evident that the derivatives synthesized demonstrate only small bathochromic shift of their spectra with respect to that of the **MEn**. It should be mentioned that the absorption and emission of the compounds **7-8** are close to that of TPD derivatives [30,31]. This observation demonstrates that the materials synthesised should show the similar values of the ionization potential (I_p) to those of the derivatives with one enamine fragment and to those of TPD derivatives.



a

b

Fig. 2. UV absorption (a) and FL (b, λ_{ex} = 350 nm) spectra of THF solutions of compounds 7 and MEn.

Transparent and stable thin amorphous films of the synthesized materials can be prepared by casting or spin coating from solutions. Electron photoemission spectra of amorphous films of compounds **7** and **8** are presented in Fig. 3. The values of I_p for the films are almost identical (ca. 5.35 eV). As it could be expected from UV absorption and FL spectroscopy data, the values of I_p of **7** and **8** are similar to those of enamines with one enamine fragment and of TPD derivatives [29-32].

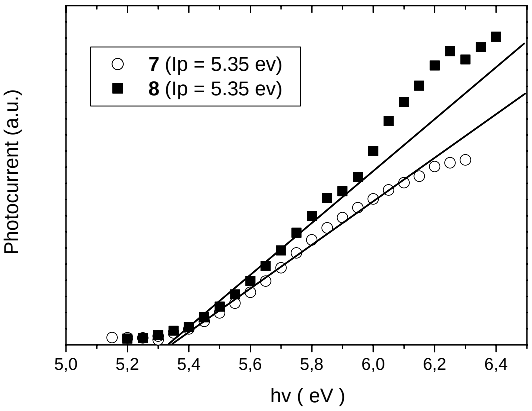


Fig. 3. Electron photoemission spectra of thin layers of 7 and 8.

The I_p level of the derivatives of N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidine suggest that these materials have potential to be used for charge transport layers of electro-photographic photoreceptors. Holes would be easily injected into the layers of the compounds synthesized from charge generation layer with I_p close to 5.35 eV. It should be mentioned that the I_p values of charge generation materials, including those widely used in electro-photographic photoreceptors pigments, such as titanyl phthalocyanines [33,34], perylene pigments [35] and bisazo pigments [36] are in the range of 5.1-5.6 eV. The I_p of the materials synthesized are also close to that of indium-tin oxide (~4.9 eV) which is used as anode in various optoelectronic devices [37]. The injection barrier of holes from the electrode into the layers of **7-8** would be ca. 0.45 eV.

Xerographic time of flight (XTOF) measurements were used to characterize the magnitudes of hole drift mobility (μ_h) for the compounds **7-8** molecularly dispersed in polymer host bisphenol Z polycarbonate (PC-Z) solutions. For the molecular dispersions of compounds **7-8** in PC-Z the room temperature μ_h shows the linear dependencies on the square root of the electric field (Fig. 4). This characteristic dependence is observed for the majority of non-crystalline organic semiconductors and can be attributed to the effects of disorder on charge transport [38].

The μ_h value of 1.3×10^{-4} cm^{2}V^{-1}s^{-1} was observed for the amorphous layer of compound **7** dispersed in PC-Z (50 %) at an electric field of 1.1×10^{6} Vcm^{-1} at 25 ºC. The layer of the molecular dispersion of compound **8** in PC-Z (67 %) showed μ_h of ca. 1.6×10^{-5} cm^{2}V^{-1}s^{-1} at an electric field of 1.9×10^{6} Vcm^{-1} at 25 ºC. The different charge transporting properties are predetermined by different concentration of the electro-active materials in the polymer host. It should be mentioned that these charge mobilities were estimated in the layers having only 33 - 50 wt.% of the electro-active material **7** or **8**. The charge mobilities higher by one or two orders of magnitude can be predicted for the amorphous films of the pure compounds.

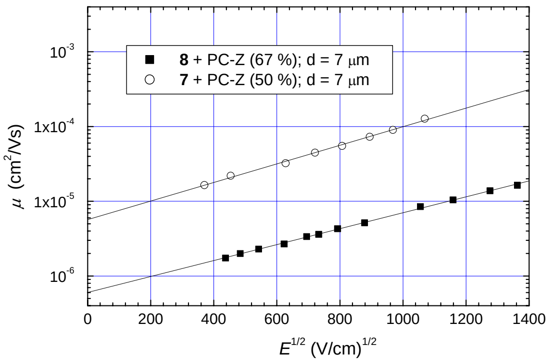


Fig. 4. Electric field dependencies of hole drift mobility in charge transport layers of the materials 7 and 8 molecularly doped in PC-Z.

In conclusion, we have synthesized the derivatives of N,N'-bis(2,2-diphenylvinyl)-N,N'-diphenylbenzidines with reactive functional groups, which form amorphous electro-active layers. The values of ionization potentials of the layers are ca. 5.35 eV. The molecular dispersions of the synthesized materials in bisphenol Z polycarbonate show time-of-flight hole mobilities reaching 10^{-4} cm^{2}V^{-1}s^{-1} at high electric fields. Low values of ionization potentials and the moderate charge transport properties of the synthesized materials show that they are potential hole-transporting materials for the application in organic optoelectronic devices.

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