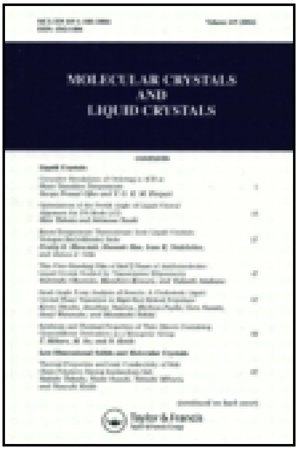

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Condensed Aromatic Amines as Electroactive Materials for Optoelectronic Applications

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Condensed Aromatic Amines as Electroactive Materials for Optoelectronic Applications

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The synthesis and properties of a series of new glass-forming condensed aromatic amines are reported. The dependence of their thermal and optical propertiess on their chemical structure is discussed. The ionization potentials of the synthesized aromatic amines measured by the electron photoemission technique are 5.30–5.40 eV. Hole drift mobilities of some derivatives molecularly dispersed in bisphenol Z polycarbonate exceed 10^{-6} *cm*^{2} *V*$^{-1}$ *s*$^{-1}$ *at high electric fields (*10^6 *V cm*$^{-1}$*), at room temperature.*

Keywords: aromatic amine; hole-drift mobility; ionization potential

INTRODUCTION

Among hole-transporting materials used in optoelectronic devices aromatic amines have attraced most attention of researchers. For

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example, aromatic amines, such as *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) [1] and 1,1-bis(di-4-tolylaminophenyl)cyclohexane (TAPC) [2], are widely used in electrophotography. Most of the modern organic electrophotographic photoreceptors have a dual-layer configuration. The main advantage of this configuration is the possibility of separate optimization of the two layers. The charge generation layer usually consists of a dye such as titanyl phthalocyanine dispersed in a polymer binder, *e.g.*, poly(vinylbutyral). The charge transport layer is usually prepared by embedding an organic hole transport material into a polymer matrix, *e.g.,* polycarbonate. A charge transport layer has to contain a large amount (up to 50%) of the active material to ensure effective transport of charges. Introduction of such a large amount of low-molar-mass charge transport compound into the polymer matrix can lead to crystallization. To prevent this problem, charge transporting compounds which do not readily crystallize are needed.

In this work we report on the synthesis and studies of new condensed aromatic amines with reactive functional groups. We also show a possibility of the preparation of hole-transporting amorphous molecular materials by twinning these compounds.

EXPERIMENTAL

Materials

The starting compounds: 9H-carbazole, diphenylamine, 4-iodoanisole, ethanethiol, epichlorohydrin, 4,4′-thiobisbenzenethiol, 1,5-dibrompentane were purchased from “Aldrich” and used as received. 3-Bromomethyl-3-methyloxetane was bought from Chemada Fine Chemicals (Israel). All the required chemicals: 18-crown-6, potassium carbonate, copper powder, potassium iodide, potassium iodate, benzyltrimethylammonium chloride (BTMA), magnesium sulphate, sodium hydride, triethylamine (TEA), potassium hydroxide, 4-dimethylaminopyridine (DMAP) were also purchased from “Aldrich”. Organic solvents were purified and dried by standard methods [3]. Silica gel was used for column chromatography.

3,6-Bis(diphenylamino)-9-(4-hydroxyphenyl)carbazole (**1**) and 3,6-bis (diphenylamino)-9-(4-(2,3-epoxypropyl)phenyloxy)carbazole (**2**) were prepared by the reported procedure [4] and the characteristics of these synthesized compounds **1** and **2** are given in our previous presentation [4].

3,6-Bis(diphenylamino)-9-(4-(3-methyloxetane-3-yl-methoxy)phenyl) carbazole (3). 0.89 g (1.5 mmol) of compound **1** was dissolved in 15 ml of ethylmethylketone and 3-bromomethyl-3-methyloxetane (8 ml) was added dropwise. After adding of 0.10 g (4.2 mmol) of NaH the reaction was carried out at 60°C for three hours. The excess of 3-bromomethyl-3-methyloxetane was removed at the reduced pressure and the resin obtained was dissolved in ethyl acetate, washed several times with water and dried over magnesium sulphate. The solvent was evaporated under vacuum and the product was purified by silica gel column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 6:1. Yield: 0.4 g (37%) of $C_{47}H_{39}N_3O_2$ (FW = 677 g/mol). MS(APCI$^+$, 20 V), m/z (%): 678 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3058, 3035 (CH_{ar}), 2957, 2929, 2867 ($CH_{aliphatic}$), 1513, 1484 ($C{=}C_{ar.}$), 1275, 1240 (C−O−C). ^{1}H NMR (300 MHz, DMSO), δ (ppm): 1.41 (s, 3H, $-C\underline{H_3}$), 4.15 (s, 2H, $-OC\underline{H_2}$), 4.34 (ds, 2H, $-OC\underline{H_2}$ etane ring), 4.54 (ds, 2H, $-OC\underline{H_2}$ in oxetane ring), 6.85–7.90 (m, 30H, aromatic protons). ^{13}C NMR (75.4 MHz, DMSO), δ (ppm): 15.01 ($-\underline{C}H_3$), 40.00 ($-\underline{C}H$), 70.38 ($-O\underline{C}H_2$), 80.39 ($-O\underline{C}H_2$ in oxetane ring), 111.04, 116.52, 120.00, 122.05, 122.31, 122.64, 123.03, 126.94, 129.59, 130.01, 139.18, 140.30, 148.74, 160.03.

Di(4-(4-(3,6-di(N,N-diphenylamino)carbazole-9)phenyloxy-2-hydroxypropylthio)phenyl)sulphide (4). 1 g (1.54 mmol) of compound **2** and 0.19 g (0.77 mmol) of 4,4′-thiobisbenzenethiol were dissolved in 15 ml of ethylmethylketone. The reaction was catalized by adding of 0.5 ml of TEA at 80°C. After 24 h the reaction was terminated by pouring the reaction mixture into methanol. The precipitated product was filtered off and purified by column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 3:2. Yield: 1.5 g (63 %) of **4**. IR (in KBr), ν/cm^{-1}: 3426 (OH), 3034 ($CH_{ar.}$), 2923, 2867 ($CH_{aliphatic}$), 1512, 1482 ($C{=}C_{ar.}$), 1272 (C−O−C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 2.67 (s, 2H, −OH), 2.71–2.73 (m, 2H, $-C\underline{H}$), 3.30–3.32 (m, 4H, $-SC\underline{H_2}$), 4.16 (s, 4H, $-OC\underline{H_2}$), 6.85–7.80 (m, 68H, aromatic protons). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 37.45 ($-S\underline{C}H_2$), 68.58 ($-\underline{C}H$), 70.40 ($-O\underline{C}H_2$), 110.73, 115.74, 118.74, 121.62, 122.71, 123.80, 125.97, 128.42, 128.48, 129.07, 130.34, 131.60, 133.94, 138.90, 140.42, 148.53, 157.53.

1,5-Di(4-(3,6-di(N,N-diphenylamino)carbazole-9)phenyloxy)pentane (5). 2 g (3.37 mmol) of compound 1, 0.366 g (1.59 mmol) of 1,5-dibromopentane and tetrabutylammonium hydrogen sulphate (0.05 g) were dissolved in ethylmethylketone (20 ml). 0.4 g (7.14 mmol) of potassium hydroxide was added stepwise and the reaction mixture was refluxed for 3 h. Then unreacted potassium hydroxide and inorganic salts were removed from the reaction mixture by filtration. The solvent was removed by rotary evaporation and the product was precipitated into methanol. The precipitated product was filtered off and purified by silica gel column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 6:1. Yield: 0.8 g ‘(40 %) of **5**. IR (in KBr), ν/cm^{-1}: 3059, 3035 ($CH_{ar.}$), 2940, 2868 ($CH_{aliphatic}$), 1512, 1484 ($C{=}C_{ar.}$), 1273, 1242 ($C-O-C$). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.36–1.56 (m, 6H, $-C\underline{H_2}$), 4.01–4.11 (m, 4H, $-OC\underline{H_2}$), 6.68–7.75 (m, 60H, aromatic protons). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 22.95 ($-OCH_2-CH_2-\underline{C}H_2-CH_2O-$), 29.05 ($-OCH_2-\underline{C}H_2-CH_2-\underline{C}H_2-CH_2O-$), 67.57 ($-O\underline{C}H_2-CH_2-CH_2-CH_2-\underline{C}H_2O-$), 110.58, 114.73, 114.98, 115.15, 122.14, 122.52, 122.93, 123.52, 127.41, 129.72, 139.19, 141.84, 148.95, 163.25.

1,3-Di(4-(3,6-di(N,N-diphenylamino)carbazole-9)phenyloxy)2-hydroxypropane (6). To the magnetically stirred solution of 0.5 g (0.84 mmol) of compound **1** in DMF, 0.54 g (0.84 mmol) of compound **2** was added. Then after several minutes 0.1 g (0.82 mmol) of DMAP was added. The reaction mixture was heated at 80°C and stirred for 48 h. After re-cooling to the room temperature it was poured into water. The precipitated crude product was filtered off and purified by silica gel column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 1:2. Yield: 0.3 g (30%) of **6**. IR (in KBr), ν/cm^{-1}: 3420 (OH), 3062, 3037 ($CH_{ar.}$), 2945 ($CH_{aliphatic}$), 1512, 1482 ($C{=}C_{ar.}$), 1269, 1250 ($C-O-C$). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 2.53 (s, 1H, $-OH$), 3.80–3.82 (m, 1H, $-C\underline{H}$), 4.40 (d, 4H, $-OC\underline{H_2}$), 6.72–7.83 (m, 60H, aromatic protons). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ (ppm): 69.53 ($-\underline{C}H$), 72.82 ($-\underline{C}H_2$), 110.53, 114.82, 114.93, 115.25, 122.21, 122.69, 122.79, 124.58, 127.82, 129.37, 139.17, 141.93, 147.53, 163.05.

Measurements

The ^1H NMR and ^{13}C NMR spectra of deuterated chloroform and deuterated dimethylsulphoxide solutions were obtained on Varian Gemini-2000 (300 MHz (^1H), 75.4 MHz (^{13}C)) spectrometer. IR spectra were recordered using Perkin Elmer FT-IR System. The spectra of solid compounds were performed in a form of KBr pellets. Electron impact mass spectra were obtained on a Waters 2Q 2000. The UV spectra were recorded on a Spectronic Genesys™ 8 spectrometer. Fluorescence emission and excitation spectra were recorded with Hitachi MPF-4 spectrometer. A 10^{-5} M solution of an investigated compound in THF was placed into microcell with an internal width of 1 mm.

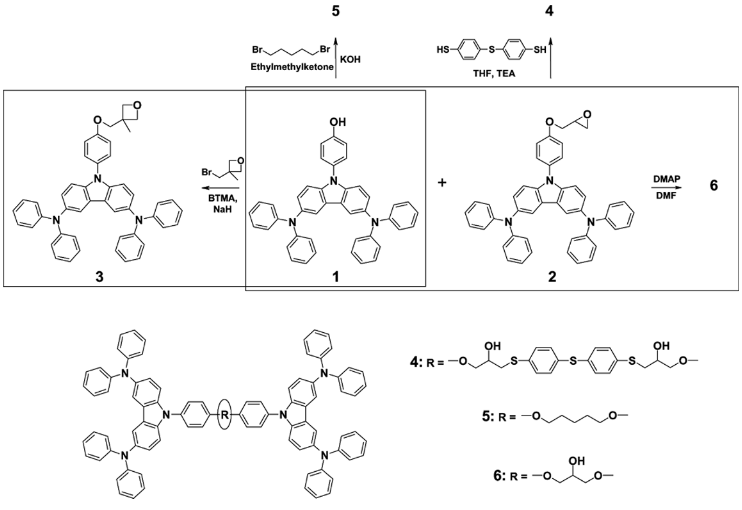
Differential scanning calorimetry (DSC) measurements were carried out with a Mettler DSC-821e and Perkin-Elmer DSC-7 at 10°C min^{-1} heating rate under nitrogen atmosphere. The glass transition temperatures (T_g) were determined from second heating scans. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA 851e at a 10°C min^{-1} heating rate under nitrogen atmosphere.

The ionization potentials (I_p) of the films of the synthesized compounds were measured by electron photoemission in air method as described before [5,6]. The standard errorr in the mean to 95% confidence for the values of ionisation potential was 0.04 eV. Hole-drift mobilities were measured by xerographic time of flight (XTOF) technique [7,8]. The samples for the measurements were prepared by casting the solutions of the molecular mixtures of the synthesized compounds with bispenol Z polycarbonate (PC-Z) at mass proportion 1:1 in THF. The substrates were polyester films with Al layer.

RESULTS AND DISCUSSION

3,6-Bis(diphenylamino)-9-(4-hydroxyphenyl)carbazole **1** and 3,6-bis (diphenylamino)-9-(4-(2,3-epoxypropyl)phenyloxy)carbazole **2** were prepared by the reported procedure [4], whereas oxetanyl substituted aromatic amine **3** was synthesized as described in Scheme 1. With the purpose of increasing molecular size, which allows to enhance the morphological stability of amorphous molecular materials we have synthesized twin-like molecules **4–6** (Scheme 1).

The structures of the newly synthesized compounds were confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy (see Experimental section). They are soluble in common organic solvents such as chloroform, tetrahydrofuran.



SCHEME 1 Synthesis of aromatic amines **3–6**.

The thermal properties of the synthesized aromatic amines were examinated by TGA and DSC in a nitrogen atmosphere. All the materials demonstrate a relatively high thermal stability, with 5% weight loss temperature (T_{ID}) exceeding 220°C, as confirmed by TGA. All synthesized aromatic amines **3–6** were isolated as amorphous materials as confirmed by DSC. When the samples of **3–6** were heated the glass-transitions were observed in a range 42–143°C and no peaks due to crystallization and melting appeared. Cooling down and the following repeated heating revealed only the glass transitions again. As an example the DSC curves of compound **5** are given in Figure 1.

The glass-transition temperatures (T_g), temperatures at which initial loss of mass (5%) was obserbed (T_{ID}), and changes in heat capacity at glass transition (ΔC_p) are summarized in Table 1.

The T_g's of the twin molecules **4** and **5** are markedly higher than that of oxetanyl substituted aromatic amine **3**. T_g of the twin compounds depends on the linking bridge. The compound **4** containing di-4-(2-hydroxypropyl)thiophenylsulphide bridge exhibit 25°C higher T_g than compound **5** containing pentane bridge.

The newly synthesized aromatic amines were also characterized by UV-vis and photoluminescence (PL) spectrometry. The maxima of the

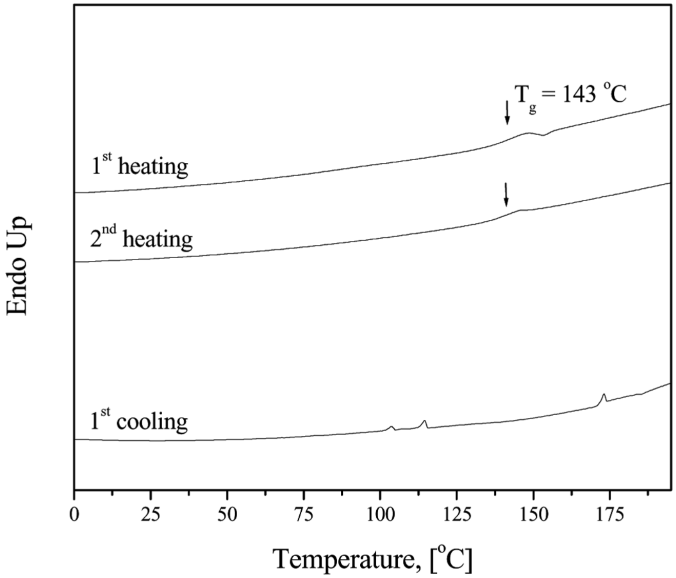


FIGURE 1 DSC curves of **5**, at the heating/cooling rate of 10°C min^{-1}, N_2 atmosphere.

TABLE 1 Thermal Characteristics of the Condensed Aromatic Amines

Compound	T_g, [°C]	ΔC_p, [J/g °C]	T_{ID}, [°C]
3	84	0.210	226
4	118	0.120	355
5	143	0.326	441
6	42	0.203	251

UV absorption and fluorescence emission spectra of dilute THF solutions of compounds **3–6** are summarized in Table 2. For the comparison the maxima of UV absorption and PL emission of 9-phenylcarbazole (**PhCz**) are given in Table 2.

Aromatic amines **3–6** absorb UV radiation in the range of 250–375 nm. The absorption spectra of compounds **3–6** are similar, due to the presence of the same chromophore. As an example, the UV-vis absorption spectra of oxetanyl substituted aromatic amine **3** and twin molecule **4** are shown in Figure 2. For a comparison the spectrum of 9-phenylcarbazole (**PhCz**) is given. The spectra of compounds **3**, **4** exhibit a bathochromic shift with respect to the spectrum of **PhCz.** Moreover, UV spectra of aromatic amine **4** show small bathochromic shift by 6 nm with respect to the spectrum of compound **3**.

The fluorescence emission spectra of dilute THF solutions of compounds **3**, **4** and **PhCz** are shown in Figure 2. The emission from aromatic amines is bathochromically shifted relative to that from 9-phenylcarbazole. The bands of fluorescence spectra of compound **4** are marginally shifted (1 nm) towards long wavelength region in comparison with that of oxetanyl substituted aromatic amine **3**. This observation is consistent with the UV spectroscopy data.

An important characteristic of electronically active compounds used in optoelectronic devices is ionization potential (I_p), which characterizes the electron releasing work under illumination. Amorphous thin films on the substrate can be prepared by casting or spin coating techniques from all aromatic amines reported in this presentation. The stabilities of the films with the thicknesses of 0.5–1 μm were sufficient for the ionization potential measurements. Figure 3 shows electron photoemission spectra of the amorphous films of compounds **3–6**. The intersection point of the straight lines drown with the absciss axis gives the values of the ionization potential, which are summarized in Table 3.

The I_p values of the synthesized compounds are rather close. They are close to I_p values of charge generation materials widely used in

TABLE 2 UV-vis Absorption (in THF solutions) and PL[a] Emission (in THF Solutions) Maxima of Compounds **3**–**6** and **PhCz**[b]

Compound	UV: λ_{max}, [nm]	PL: λ_{max}, [nm]
3	304. 352[c]	432. 450[c]
4	310. 358[c]	433. 452[c]
5	304. 352[c]	430. 450[c]
6	302. 350[c]	429. 448[c]
PhCz	293. 340	350. 363

[a] For **3** and **4** excitation wavelength 310 nm, for **PhCz** - 290 nm.
[b] 10^{-5} mol l$^{-1;}$
[c] Shoulder.

electrographic photoreceptors such as titanyl phthalocyanines, perylene pigments and bisazo pigments (5.1–5.6 eV) [9]. This observation shows that the synthesized compounds can be used as charge transport materials in electrophotographic photoreceptors.

The room temperature electric field dependencies of hole drift mobility (μ) values for the solid solutions of the synthesized aromatic amines in PC-Z are given in Figure 4. The linear dependencies of the hole-drift mobility on the square root of the electric field E are

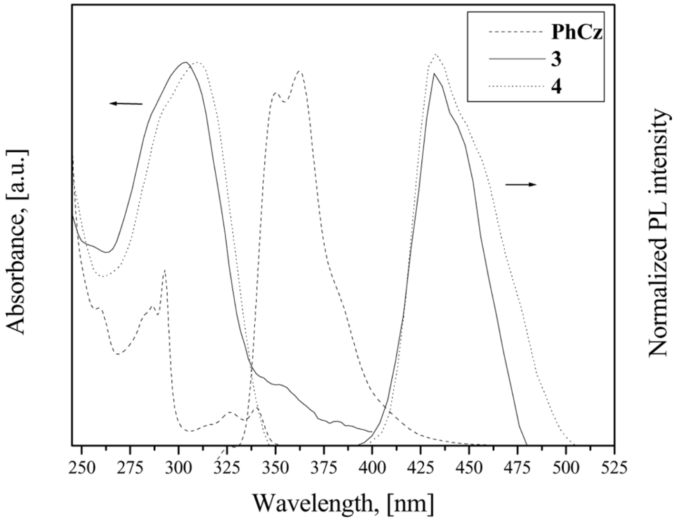


FIGURE 2 UV-vis absorption and normalized PL emission spectra of **3**, **4** and 9-phenylcarbazole (**PhCz**) dilute THF solutions (10^{-5} mol l^{-1}).

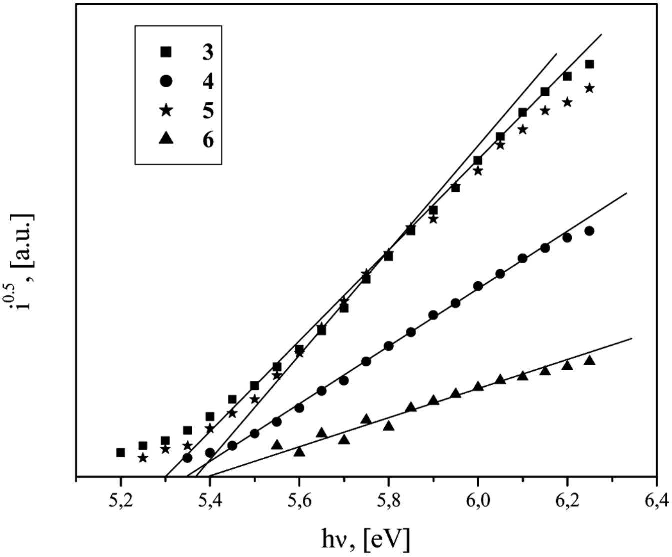


FIGURE 3 The electron photoemission spectra in air of the films of aromatic amines **3**–**6**.

observed. In all the cases drift mobility may be well approximated by the formula $\mu = \mu_0 \exp(\alpha\sqrt{E})$, here α is Pool-Frenkel parameter.

Such dependencies of charge mobility on electrical field are characteristic of many organic photoconductors and are predicted by the Bässler-Borsenberger model [2,10]. The solid solutions of aromatic amines **3**–**6** in PC-Z (mass proportion 1:1) demonstrated hole drift mobility values in a range from $9.0 \cdot 10^{-8}$ to $2.0 \cdot 10^{-6}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ at electric field $E = 6.4 \cdot 10^5\,\mathrm{V\,cm}^{-1}$, at room temperature (Table 4). Among the compounds synthesized the compound **4** showed the best charge transport properties. Hole mobilities of its 50% solid solutions in PC-Z even exceeded those of the analogous system containing compound **3**, although the concentration of electrophores in **3** is

TABLE 3 Ionization Potentials of the Films of the Condensed Aromatic Amines

Compounds	**3**	**4**	**5**	**6**
I_p, [eV]	5.30	5.36	5.37	5.40

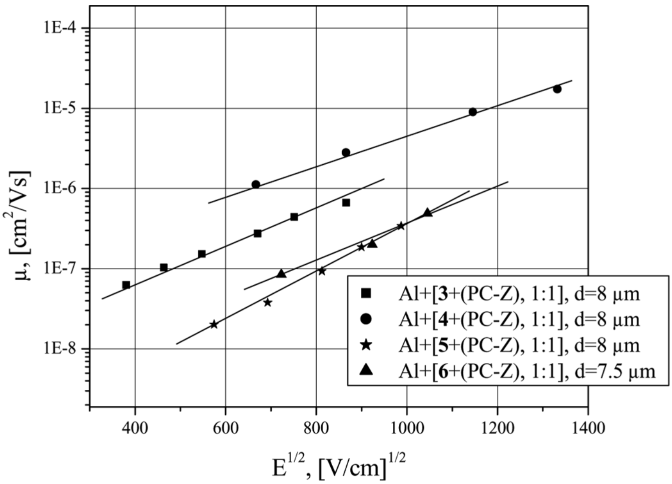


FIGURE 4 Electric field dependencies of the hole drift mobilities (μ) in charge transport layers of compounds **3**–**6** doped in PC-Z (mass proportion 1:1).

higher. This observation can apparently be explained by the presence of electron rich sulphur atoms in **4**.

In conclusion, new condensed aromatic amines were synthesized and investigated as potential charge-transport materials for optoelectronics. The thermal, optical and photoelectrical properties of the synthesized compounds were studies. The synthesized aromatic amines form glasses with the glass transition temperatures in the range of 42–143°C as characterized by differential scanning calorimetry. The electron photoemission spectra of the synthesized compounds have been recorded and the ionization potentials of 5.30–5.40 eV have been established. Room temperature hole drift mobilities

TABLE 4 Hole Mobility Data

Composition	d, [μm]	μ_0^*, [cm^2/Vs]	μ^{**}, [cm^2/Vs]	α^{***}, [cm/V]$^{1/2}$
Al + [**3** + (PC-Z), 1:1]	8	$1.0\cdot10^{-8}$	$5.1\cdot10^{-7}$	0.0049
Al + [**4** + (PC-Z), 1:1]	8	$6.4\cdot10^{-8}$	$2.0\cdot10^{-6}$	0.0043
Al + [**5** + (PC-Z), 1:1]	8	$3.3\cdot10^{-10}$	$9.0\cdot10^{-8}$	0.007
Al + [**6** + (PC-Z), 1:1]	7.5	$1.2\cdot10^{-9}$	$1.2\cdot10^{-7}$	0.0053

μ_0^* – zero field mobility.
μ^{**} – drift mobility values at electric field $E = 6.4\cdot10^5\,\mathrm{V\,cm^{-1}}$.
α^{***} – Pool-Frenkel parameter.

in 50% solid solutions of some synthesized compounds in bisphenol Z polycarbonate established by the xerographic time-of-flight technique was found to exceed $10^{-6}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ at high electric fields ($10^6\,\mathrm{V\,cm}^{-1}$).

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