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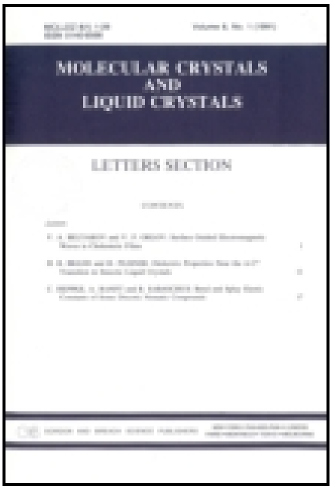

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# Hole-Transporting Carbazole-Based Imines

Jurate Simokaitiene [a] , Saulius Grigalevicius [a] , Juozas Vidas Grazulevicius [a] , Vygintas Jankauskas [b] & Jonas Sidaravicius [c]

[a] Department of Organic Technology , Kaunas University of Technology, Radvilenu plentas, LT , Kaunas , Lithuania

[b] Department of Solid State Electronics , Vilnius University, Sauletekio aleja, LT , Vilnius , Lithuania

[c] Department of Polygraphic Machines , Vilnius Gediminas Technical University LT , Vilnius , Lithuania

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# Hole-Transporting Carbazole-Based Imines

JURATE SIMOKAITIENE,[1] SAULIUS GRIGALEVICIUS,[1] JUOZAS VIDAS GRAZULEVICIUS,[1] VYGINTAS JANKAUSKAS,[2] AND JONAS SIDARAVICIUS[3]

[1]Department of Organic Technology, Kaunas University of Technology, Radvilenu plentas, LT, Kaunas, Lithuania
[2]Department of Solid State Electronics, Vilnius University, Sauletekio aleja, LT, Vilnius, Lithuania
[3]Department of Polygraphic Machines, Vilnius Gediminas Technical University LT, Vilnius, Lithuania

*Carbazole-based imines were synthesized by the reactions of 3-amino-9-ethylcarbazole with heteroaromatic aldehydes (3-formyl-9-ethylcarbazole or 3-formyl-10-(2-ethylhexyl)phenothiazine) or with 4,4′-bis(dimethylamino)benzophenone. The characterization of the derivatives synthesized by* $^1H$ *NMR and IR spectroscopy as well as by MS spectrometry is presented. The electron photoemission spectra of thin layers of the materials were recorded and the ionization potentials of ca 5.3 eV were established. Hole drift mobilities in the layers of bisphenol Z polycarbonate containing 50% of the electro-active material reached* $4 \times 10^{-6}$ *cm*$^2$*/Vs at an electric field of* $1.4 \times 10^6$ *V/cm.*

**Keywords** Carbazole; hole drift mobility; imine; ionization potential; molecular glass

## Introduction

Low molecular weight organic compounds that form glasses are called molecular glasses or amorphous molecular materials. Electroactive molecular glasses show excellent processability, transparency, isotropic and homogeneous properties and receive growing attention both in terms of academic interest and technological applications [1]. Glass-forming aromatic amines, heterocyclic compounds, hydrazones, enamines belong to the class of hole-transporting materials and are known for various applications such as electrophotographic photoreceptors, organic light-emitting diodes, photovoltaic cells [2–8]. Aromatic imines were also reported as potential electroactive materials [9,10], however their charge-transporting properties, to our knowledge, were not studied.

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Address correspondence to Juozas Vidas Grazulevicius, Department of Organic Technology, Kaunas University of Technology, Radvilenu plentas 19, LT-50254, Kaunas, Lithuania. E-mail: juozas.grazulevicius@ktu.lt

For the purpose of developing of electronically active molecular glasses, we have reported previously several series of carbazole and [3,3′]bicarbazole-based derivatives [11–14]. In the present study we report on the synthesis and optical, photophysical as well as photoelectrical properties properties of new carbazole based imines.

## Experimental

### *Instrumentation*

$^1$H NMR spectra were recorded using Varian Unity Inova and JOEL JNM- F × 100 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 Hitachi MPF-4 spectrometer.

The ionization potentials ($I_p$) of the materials were measured by the electron photoemission in air method [15]. The details of the $I_p$ measurements were reported earlier [16].

Hole drift mobilities were measured by the xerographic time of flight technique [17,18]. The samples for the charge carrier mobility measurements were prepared by procedure as described earlier [19].

### *Materials*

10H-phenothiazine (**1**), 3-amino-9-ethylcarbazole (**4**), 3-formyl-9-ethylcarbazole (**5**), 4,4′-bis(dimethylamino)benzophenone, (Michler's ketone, **6**), 1,4-diazabicyclo[2.2.2]-octane, $POCl_3$ and $TiCl_4$ were purchased from Aldrich and used as received.

10-(2-Ethylhexyl)phenothiazine (**2**) was prepared by the similar procedure as described in literature [20]. 10H-phenothiazine (20 g, 0.1 mol), 1-bromo-2-ethylhexane (38.6 g, 0.2 mol) and tetrabutylammonium hydrogen sulphate (0.2 g, 0.6 mmol) were heated to reflux in 300 ml of dry toluene and then powdered potassium hydroxide (8.4 g, 0.15 mol) was added. The reaction mixture was refluxed for 12 h. After the reaction the cooled mixture was filtered, washed thoroughly with water, dried over anhydrous sodium sulphate and the solvent was removed by evaporation. The residue was fractionally distilled at high vacuum. The yield of **2** (yellowish oil) was 24 g. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$, ppm: 0.93 (t, J = 6.8 Hz, 3H, $CH_3$); 0.93 (t, J = 7.4 Hz, 3H, $CH_3$); 1.30–1.55 (m, 8H, $CH_2$); 1.92–2.08 (m, 1H, CH); 3.79 (d, 2H, J = 6.8 Hz,$CH_2$-N); 6.89–7.26 (m, 8H, Ar). IR (KBr), $cm^{-1}$: 3066; 2958, 2927, 2857; 1594, 1571; 1285. MS(APCI$^+$, 20 V), m/z, %: 312 ([M+H]$^+$, 95).

3-Formyl-10-(2-ethylhexyl)phenothiazine (**3**) was synthesized from compound **2** by Vilsmeier formylation reaction [21]. $POCl_3$ (1.47 ml, 16 mmol) was added drop wise to dry DMF (3.7 ml, 48 mmol) at 0°C under nitrogen atmosphere. 10-(2-Ethylhexyl)phenothiazine (4.98 g, 16 mmol) was added to the reaction flask. The reaction mixture was stirred at 85°C until the starting compound fully reacted. 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 product was filtered off. The crude product separated by filtration was further purified by silica gel column chromatography using hexane/ethyl acetate (vol. ratio 3:1) as an eluent. The yield of **3** (yellow amorphous resin) was 0.74 g. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$, ppm: 0.62–0.95 (m, 6H, $CH_3$); 1.00–1.44 (m, 8H, $CH_2$); 1.70–2.10 (m, 1H, CH); 3.94 (d, 2H, *J* = 7,3 Hz, $CH_2$-N); 7.10–8.50 (m, 7H, ar); 9.97 (s, 1H, CHO). IR

(KBr), $cm^{-1}$: 3053; 2957, 2926, 2849; 1687; 1586; 1230. MS($APCI^+$, 20 V), m/z, %: 308 ($[M+H]^+$, 100).

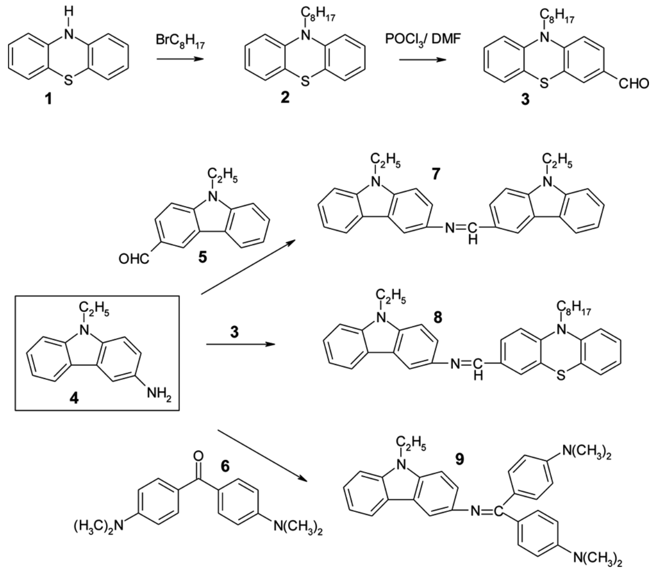
3-(9-Ethylcarbazol-3-yl-iminomethyl)-9-ethylcarbazole (**7**). 3-Formyl-9-ethylcarbazole (**5**) (1.0 g, 4.48 mmol) and 3-amino-9-ethylcarbazole (**4**) (1.4 g, 96.7 mmol) were dissolved in 10 ml of ethanol. The mixture was refluxed under $N_2$ for 24 h. Then the reaction mixture was cooled down, the product precipitated out and was recovered by filtration. The yield of **7** (of yellow amorphous material) was 1.6 g. $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$, ppm: 0.36 (t, 6H, $CH_3$); 4.10–4.34 (m, 4H, $CH_2$); 7.11–8.64 (m, 14H, ar); 8.75 (s, 1H, N=CH). IR (KBr), $cm^{-1}$: 3048, 2967, 2863, 1627; 1614; 1597, 1472, 1447, 1281, 1238, 1153, 1132, 1121, 842, 819, 803, 783, 766, 744, 726. MS($APCI^+$, 20 V), m/z, %: 416 ($[M+H]^+$, 100).

3-(9-Ethylcarbazol-3-yl-iminomethyl)-10-(2-ethylhexyl)phenothiazine (**8**). 3-Formyl-10-(2-ethylhexyl)phenothiazine (**3**) (0.89 g, 2.6 mmol) and 3-amino-9-ethylcarbazole (**4**) (0.82 g, 3.9 mmol) were dissolved in 30 ml of methanol. The reaction mixture was refluxed under $N_2$ for 2 h. Then the solvent was distilled under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/ethyl acetate (vol. ratio 7:1) as an eluent. The yield of **8** (yellow amorphous material) was 0.4 g. $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$, ppm: 0.86–1.02 (m, 6H, $CH_3$); 1.41–1.61 (m, 8H, $CH_2$); 1.73–1.90 (m, 1H, CH); 1.95–2.13 (t, 3H, N-$CH_2$-$\underline{CH_3}$); 3.80–3.88 (d, 2H, N-$\underline{CH_2}$-CH; 4.36–4.46 (q, 2H, N-$\underline{CH_2}$-$CH_3$); 6.95–8.23 (m, 14H, ar); 8.58 (s, 1H, $\underline{N}$=CH). IR (KBr), $cm^{-1}$: 3058, 2959, 2826, 2857, 1633, 1612, 1598, 1573, 1460, 1333, 1249, 1238, 1227, 1162, 1334, 1123, 1102, 780, 764, 747, 727. MS($APCI^+$, 20 V), m/z, %: 532 ($[M+H]^+$, 100).

N-[Bis(4-dimethylaminophenyl)methylidene]-N-(9-ethylcarbazol-3-yl)amine (**9**). 3-Amino-9-ethylcarbazole (**4**) (0.6 g, 2.85 mmol), 4,4′-bis(dimethylamino)benzophenone (**6**) (1.54 g, 5.7 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.96 g, 8.56 mmol) were dissolved in 40 ml of 1,2-dichlorobenzene. Then $TiCl_4$ (0.86 g, 4.55 mmol) was added drop-wise to the solution. The reaction mixture was stirred at 130°C under $N_2$ for 24 h. Then the reaction mixture was cooled down to the room temperature, 1,4-diazabicyclo[2.2.2]octane precipitated out and was removed by filtration. Then hexane was added to the solution and excess of **6** precipitated out. When the precipitate was filtered off, the solvents were distilled under reduced pressure and the crude product was purified by silica gel column using hexane/acetone (vol. ratio 1:6) as an eluent. The yield of **9** (orange amorphous material) was 0.32 g. $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$, ppm: 1.38–1.48 (t, 3H, $CH_3$); 2.94 (s, 6H, $CH_3$); 3.18 (s, 6H, $CH_3$); 4.33–4.38 (q, 2H, $CH_2$) 6.53–8.10 (m, 15H, ar). IR (KBr), $cm^{-1}$: 3447, 3041, 2888, 2859, 2807, 1869, 1737, 1712, 1609, 1584, 1360, 1276, 12428, 1211, 1190, 1182, 1168, 1137, 1120, 823, 811, 782, 749, 685. MS($APCI^+$, 20 V), m/z, %: 461 ($[M+H]^+$, 100).

## Results and Discussion

Carbazole-based imines (**7**–**9**) were prepared as described in Scheme 1 via the nucleophilic addition reaction of the commercially available 3-amino-9-ethylcarbazole (**4**) with an excess of the corresponding aldehyde (**3** or **5**) or ketone **6**. The reactions of amine with the aldehydes proceeded without catalyst. $TiCl_4$ and 1,4-diazabicyclo[2.2.2]octane were used for the acceleration of the reaction between **4** and 4, 4′-bis(dimethylamino)benzophenone (**6**). The starting aldehyde 3-formyl-10-(2-ethylhexyl)phenothiazine (**3**) was prepared from 10H-phenothiazine (**1**) by two step



Scheme 1. The preparation of carbazole-based imines (**7**–**9**).

synthesis. The first step was alkylation of **1** with 2-ethylhexylbromide under basic conditions to get alkyl substituted derivative **2**. Vilsmeier reaction [21] of compound **2** with phosphoryl chloride afforded 3-formyl-10-(2-ethylhexyl)phenothiazine (**3**).

All the newly synthesized compounds were identified by mass spectrometry, IR and $^1$H NMR spectrometries. The data were found to be in good agreement with the proposed structures. Carbazole-based imines (**7**–**9**) were readily soluble in common organic solvents at the room temperature. Transparent thin amorphous films of these materials could be prepared by casting or spin coating from solutions.

UV absorption and FL spectra of dilute THF solutions of the compounds synthesized were recorded. The wavelengths of the absorption and emission maxima ($\lambda_{max}$) are collected in Table 1. The characteristics of 9-ethylcarbazole (**EtCz**) are presented for the comparison in Table 1. The electronic absorption energy of compounds **7**–**9** is comparable, and the $\lambda_{max}$ values are in the range of 242–389 nm. Their FL emission maxima appear in the region of wavelengths from 418 to 436 nm.

The lowest energy absorption maxima of compounds **7**–**9** are red shifted with respect of the corresponding maxima of **EtCz** or of 9,9′-dialkyl-[3,3′]bicarbazolyl

**Table 1.** UV absorption and FL emission maxima of **7–9** and **EtCz**

| Compound | FL[a]: $\lambda_{max}$ (nm) | UV[a]: $\lambda_{max}$ (nm) |
|---|---|---|
| 7 | 424 | 245, 296, 349 |
| 8 | 436 | 262, 294, 389 |
| 9 | 418 | 242, 324, 352 |
| EtCz | 349, 367 | 259, 290, 329, 342 |

[a]Concentration $10^{-5}$ mol l$^{-1}$. Excitation wavelength 295 nm.

[22]. The highest bothochromic shift was observed for the phenothiazinyl-containing derivative **8**. FL spectrum of imine **7** containing two carbazolyl fragments and for the comparison that of **EtCz** are presented in Figure 1. The spectrum of **7** is considerably red shifted with respect of that of **EtCz**. The similar shifts were observed for **8** and **9**. The red shifts of absorption and fluorescence spectra of the synthesized compounds with respect of those of **EtCz** demonstrate that the new compounds are $\pi$- conjugated through the lone electron pair at the nitrogen atom of imine fragment and that $\pi$-electrons are delocalised over these molecules. In the same manner with the red shift of UV absorption, which is interpreted as the extended conjugation, stabilizing the oxidized state of the compounds, they should show lower values of ionization potential ($I_p$) than 9-alkylcarbazole or polymers containing pendant carbazolyl groups.

Electron photoemission spectra of the layers of compounds (**7**–**9**) are presented in Figure 2. The values of $I_p$ of the layers of the compounds are very close and do not exceed 5.35 eV. This value is by more tha 0.4 eV lower than that of derivatives having electronically isolated carbazolyl groups [23].

Holes would be easily injected into the layers of the synthesized materials from a charge generation layer or a conductive anode with $I_p$ or work function close to 5.3 eV. The $I_p$ values of charge generation materials, including those widely used in electrophotographic photoreceptors such as titanyl phthalocyanines [24,25], perylene pigments [26] and bisazo pigments [27] are in the range of 5.1–5.6 eV. The $I_p$ of the materials (**7–9**) is also close to that of indium-tin oxide (~4.9 eV) which is used as anode in various optoelectronic devices [28]. The injection barrier of holes from an electrode into the layers of **7–9** would be ca. 0.4 eV.

Compounds **7** and **8** having the best solubility in polymer host bisphenol Z polycarbonate (PC-Z) solutions were used for charge transport studies. Xerographic time of flight (XTOF) measurements were used to characterize the magnitudes of hole drift mobility ($\mu_h$) for the compounds molecularly dispersed in PC-Z. Transit time for the samples with the hole-transporting materials was determined by the braking point on the dU/dt transient in double logarithmic scale (Fig. 3). The character of

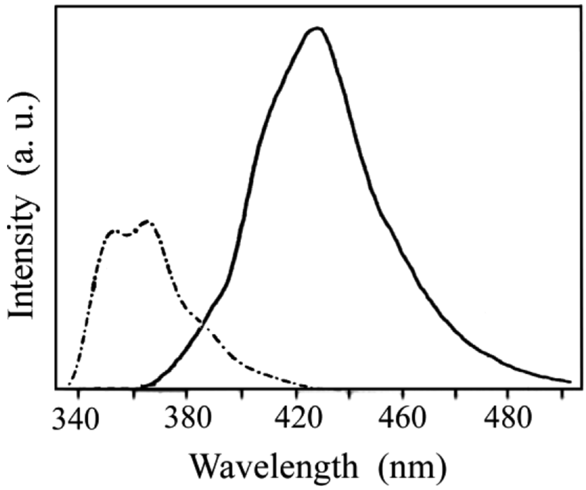


**Figure 1.** FL spectra of THF dilute solutions of **7** (solid line) and of **EtCz** (dotted line).

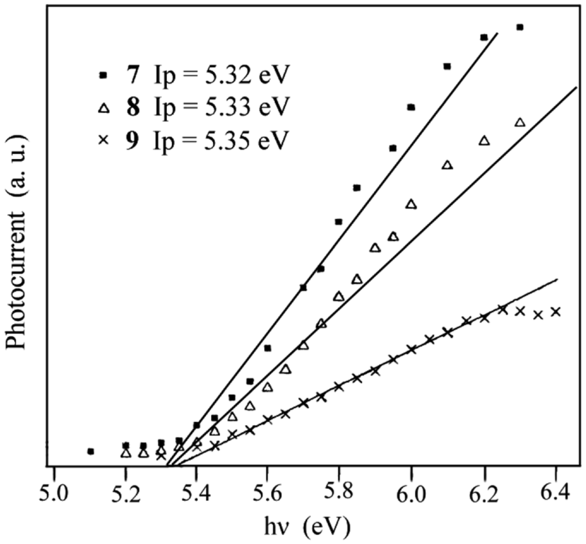


**Figure 2.** Electron photoemission spectra of thin layers of compounds **7–9**.

XTOF transients given in Figure 3 shows that dispersive charge transport is characteristic of the molecular dispersion of **7** in PC-Z.

For the molecular dispersions of compounds **7, 8** in PC-Z the room temperature hole mobilities show the linear dependencies on the square root of the electric field (Fig. 4.). This is characteristic dependence for the majority of non-crystalline organic semiconductors and can be attributed to the effects of disorder on charge transport [8]. The $\mu_h$ value of $1.6 \times 10^{-8}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ was observed for the amorphous layer of compound **7** dispersed in PC-Z at an electric field of $1.4 \times 10^6\,\mathrm{V\,cm^{-1}}$ at 25°C. The layer of the molecular dispersion of compound **8** in PC-Z showed higher $\mu_h$ of ca. $4 \times 10^{-6}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at an electric field of $1.35 \times 10^6\,\mathrm{V\,cm^{-1}}$. The different charge

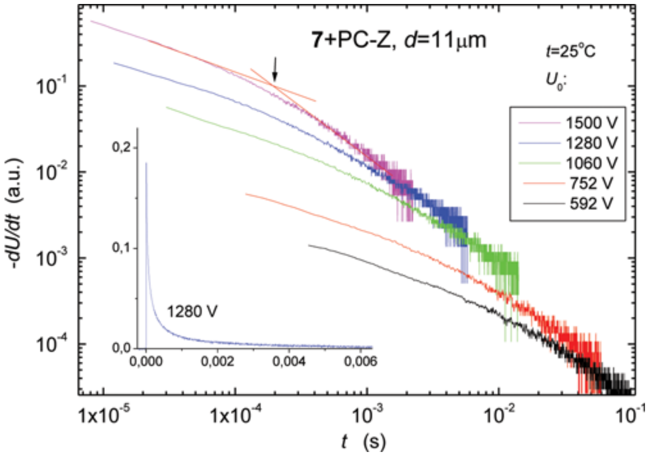


**Figure 3.** XTOF transients of **7** doped in PC-Z (50%), insert shows one of the transient curves in linear plot.

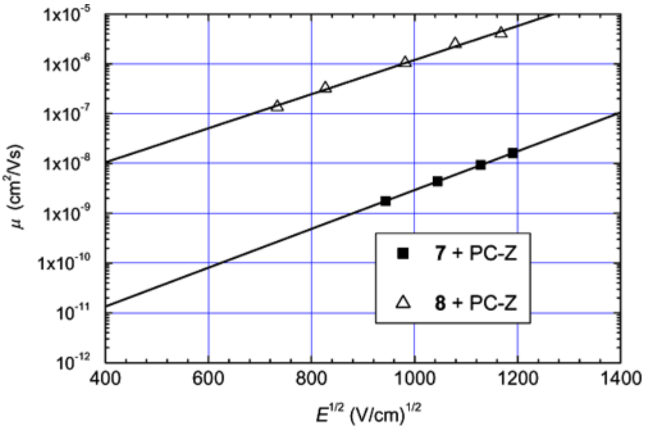


**Figure 4.** Electric field dependencies of hole drift mobility in charge transport layers of **7** and **8** molecularly doped in PC-Z (50%).

transporting properties can be predetermined by chemical structure of the compounds as well as by distribution of the molecules in the polymer host.

In conclusion, we have synthesized series carbazole-based imines, the layers of which demonstrate rather low ionization potentials of ca 5.3 eV. The molecular dispersions of the synthesized materials in bisphenol Z polycarbonate show time-of-flight hole mobilities reaching $4 \times 10^{-6}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at an electric field of $1.35 \times 10^6\,\mathrm{V\,cm^{-1}}$ 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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