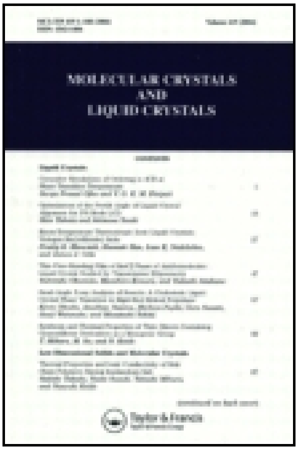

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# Hole-Transporting Glass-Forming 3,3′-Dicarbazyl-Based Hydrazones

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# Hole-Transporting Glass-Forming 3,3′-Dicarbazyl-Based Hydrazones

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*3,3′-Di(9-(4-butylphenyl)carbazyl) and 3,3′-di(9-ethylcarbazyl)-based hydrazones were synthesized by the multi-step synthetic route including oxidative dimerization of 9-(4-butylphenyl)carbazole and 9-ethylcarbazole, formylation of the dimers obtained and the reactions of the formyl derivatives with different hydrazines. The chemical structure of the compounds was confirmed by* $^1$*HNMR, IR and mass spectroscopy. The hydrazones synthesized form stable glasses with the glass transition temperatures exceeding 140°C. The values of ionisation potentials measured by electron photoemission technique are in the range of 5,21–5,4 eV. The hole drift mobilities in the films of the 50% solid solutions of the hydrazones in*

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*bisphenol Z polycarbonate established by the xerographic time-of-flight technique exceed $10^{-5}$ $cm^2/Vs$ at high electric fields.*

**Keywords:** carbazole; glass-forming; hole transport; hydrazone

## INTRODUCTION

Charge-transporting molecular glasses represent a rapidly expanding subject of research because of their present or potential application in various electronic and optoelectronic devices. The aim of our work was synthesis and investigation of the properties of hole-transporting compounds, which would be stable in amorphous phase. Such compounds themselves would be able to form amorphous films on the substrates and their concentration in molecularly doped polymers could be considerably increased. One of the ways to increase the morphological stability of molecular glasses is to increase the size of molecules. Increase of the size of the molecule usually also leads to the enlargement of the system of conjugated $\pi$-electrons, which allows to expect enhanced charge carrier mobilities. In this work we have chosen ethylcarbazole and phenylcarbazole dimers as the main building blocks for the design and synthesis of hole-transporting and film-forming hydrazones. This choice was based on our earlier reported observations of high hole drift mobilities in the amorphous films of phenylcarbazole-based hydrazones and aromatic amines [1,2].

## EXPERIMENTAL

### Materials

9H-carbazole, 9-ethylcarbazole, 1-bromo-4-butylbenzene, N,N-di phenylhydrazine hydrochloride, 1-methyl-1-phenylhydrazine, 18-crown-6 were purchased from “Aldrich” and used as received without further purification. Phosphorus oxichloride was purchased from “Riedel–de Haen” and used as received without further purification.

### *9-(4-Butylphenyl)-9H-Carbazole (1a)*

4 g (23.9 mmol) of 9H-carbazole, 7.87 g (36.8 mmol) of 1-bromo-4-butylbenzene, 11.23 g (81.3 mmol) of powdered anhydrous potassium carbonate, 3.11 g (47.8 mmol) of copper powder and 1.26 g (4.8 mmol) of 18-crown-6 were refluxed in 1-nitrobenzene (30 ml) under nitrogen for 8 hours. Then copper and inorganic salts were removed by

filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and the crude product was purified by aluminium oxide column chromatography (ethyl acetate/n-hexane = 1:20) and recrystalized from the eluent to yield 4.29 g (60%) of yelowish crystals (m.p.: 86°C). $^1$H NMR (100 MHz, $CDCl_3$, $\delta$, ppm) 0.95 (t, 3 H, $J = 6.5$ Hz, $CH_3$), 1.2–1.87 (m, 4 H, $2CH_2$), 2.72 (t, 2 H, $J = 7.5$ Hz, $NCH_2$), 7.15–7.57 (m, 10 H, ar), 8.14 (d, 2 H, $J = 9$ Hz, ar). IR (in KBr), $\nu/cm^{-1}$: 3050 ($CH_{ar}$), 2940 ($CH_{aliphatic}$), 1580, 1500 ($C{=}C_{ar}$), 700 ($CH_{ar}$).

### 9,9′-(4-Butylphenyl)-3,3′-Dicarbazyl (2a)

1.2 g (4.01 mmol) 9-(4-butylphenyl)-9H-carbazole **(1a)**, 2.68 g (16.04 mmol) of $Fecl_3$ were added to 25 ml of dry chloroform. After stirring at ambient temperature for 1 h, the reaction mixture was poured into methanol. The precipitated product was filtered and washed with methanol. White powder was obtained after several reprecipitations into methanol. It was dried under vacuum. Additionally it was purified using silica gel column chromatography (ethyl acetate/n-hexane). Yield: 0.8 g (67%) of yellowish amorphous solid. $^1$H NMR (250 MHz, $CDCl_3$, $\delta$, ppm) 1.02 (t, 3 H, $J = 7.4$ Hz, $CH_3$), 1.39–1.55 (m, 2 H, $2CH_2$), 1.74 (p, 2 H, $J = 8$ Hz, $CH_2$), 2.77 (t, 2 H, $J = 7.7$ Hz, $PhCH_2$), 7.35–7.6 (m, 16 H, ar), 7.77 (m, 2 H, ar), 8.25 (d, 2 H, $J = 7.5$ Hz, ar), 8.47 (s, 2 H, ar). IR (in KBr), $\nu/cm^{-1}$: 2920 ($CH_{aliphatic}$), 1600, 1520, 1460 ($C{=}C_{ar}$).

### 9,9′-Diethyl-3,3′-Dicarbazyl (2b)

Was synthesised by the same procedure as **2a** described above. Yield: 4.68 g (92%). $^1$H NMR (250 MHz, $CDCl_3$, $\delta$, ppm) 1.47 (t, 6 H, $2CH_3$), 4.35–4.50 (m, 4 H, $2CH_2$), 7.20–7.30 (m, 2 H, ar), 7.40–7.60 (m, 6 H, ar), 7.83 (d, 2 H, ar), 8.20 (d, 2 H, ar), 8.40 (s, 2 H, ar). IR (in KBr), $\nu/cm^{-1}$: 3050 ($C–H_{ar}$), 2980 ($CH_{aliphatic}$), 1605, 1490 ($C{=}C_{ar}$).

### 9,9′-(4-Butylphenyl)-3,3′-Dicarbazyl-6,6′-Carbaldehyde (3a)

3.1 g (0.02 mol) of $POCl_3$ were added dropwise to 1.75 g (0.021 mol) of DMF at 0°C ($N_2$ atmosphere). 2.5 g (0.004 mol) of 9,9′–(4-butylphenyl)-3,3′-dicarbazyl (**2a**) were dissolved in DMF and added to the prepared complex. The reaction mixture was stirred at 70°C for 72 h. Then it was poured into ice water and neutralized with sodium acetate and extracted with chloroform. The extract was dried over magnesium sulphate and after evaporation of the solvent the crude product was purified by silica gel column chromatography (ethyl acetate/hexane). After the purification it was obtained 1.9 g (67%) of brownish powder. $^1$H NMR (100 MHz, $CDCl_3$, $\delta$, ppm) 0.99 (t, 6 H, $2CH_3$), 1.1–1.9 (m, 8 H, $4CH_2$), 2.76( t, 4 H, $2CH_2$), 7.45–7.65 (m, 10 H, ar), 7.76 (d, 2 H, ar), 7.84

(d, 2 H, ar), 8.46 (s, 2 H, ar), 8.70 (s, 2 H, ar), 10.01 (s, 2 H, CHO). IR (in KBr), $\nu$/cm$^{-1}$: 3034 (CH$_{ar}$), 2953, 2926 (CH$_{aliphatic}$), 1684 (C=O), 1595, 1515, 1445 (C=C$_{ar}$), 803 (CH$_{ar}$).

### *9,9′-Diethyl-3,3′-Dicarbazyl-6,6′-Carbaldehyde (3b)*

The dicarbaldehyde was synthesised by the same procedure as **3a** described above. 9,9′-diethyl-3,3′-dicarbazyl (**2b**) was used as a starting compound. The yield was 38% of brownish crystals. $^1$H NMR (100 MHz, CDCl$_3$, $\delta$, ppm) 1.53 (t, 6 H, 2CH$_3$), 4.40–4.50 (m, 4 H, 2CH$_2$), 7.45–7.65 (m, 4 H, ar), 7.90 (d, 2 H, ar), 8.05 (d, 2 H, ar), 8.45 (s, 2 H, ar), 8.70 (s, 2 H, ar), 10.10 (s, 2 H, CHO). IR (in KBr) $\nu$/cm$^{-1}$: 3050 (C–H$_{ar}$), 2940 (CH$_{aliphatic}$), 1690 (C=O), 1600, 1495 (C=C$_{ar}$).

### *9,9′-(4-Butylphenyl)-3,3′-Dicarbazyl-6,6′-Carbaldehyde N,N-Diphenylhydrazone (4a′)*

0.5 g (1.18*10$^{-3}$ mol) of 9,9′-(4-butylphenyl)-3,3′-dicarbazyl-6,6′-carbaldehyde (**3a**) were dissolved in 1 l of 2-propanol under heating and this solution was added dropwise to the solution of 0.8 g (4.7*10$^{-3}$mol) of 1,1-diphenylhydrazine hydrochloride in 10 ml of methanol. The reaction mixture was stirred for 1 h at the room temperature. Then it was filtered and the crude product was purified by flash chromatography (n-hexane/CHCl$_3$). The yield was 0.14 g (19%) of yellowish amorphous material. $^1$H NMR (100 MHz, CDCl$_3$, $\delta$, ppm) 1.0 (t, 6 H, $J$ = 7 Hz, 2CH$_3$), 1.2–1.9 (m, 8 H, 4CH$_2$), 2.76 (t, 4 H, $J$ = 7.7 Hz, 2NCH$_2$), 7.1–7.95 (m, 38 H, ar), 8.32 (s, 2 H, ar), 8.42 (s, 2 H, ar). IR (in KBr) $\nu$/cm$^{-1}$: 3070, 3035 (C–H$_{ar}$), 2970, 2930 (CH$_{aliphatic}$), 1600, 1495 (C=C$_{ar}$). MS (m/z): 985 (M$^+$).

### *9,9′-(4-Butylphenyl)-3,3′-Dicarbazyl-6,6′-Carbaldehyde N-methyl-N-Phenylhydrazone (4a)*

Was synthesized by the same procedure as **4a**′ except the different solvent. Chloroform was used as a solvent. The yield was 23% of yellowish amorphous material. $^1$H NMR (100 MHz, CDCl$_3$, $\delta$, ppm) 0.99 (t, 6 H, $J$ = 6.9 Hz, 2CH$_3$), 1.2–1.9 (m, 8 H, 4CH$_2$), 2.74 (t, 4 H, $J$ = 7.3 Hz, 2NCH$_2$), 3.44 (s, 6 H, 2NCH$_3$), 6.75–7.05 (m, 2 H, ph), 7.2–8.0 (m, 28 H, ar), 8.47 (s, 2 H, ar). IR (in KBr) $\nu$/cm$^{-1}$: 3030 (C–H$_{ar}$), 2970, 2930 (CH$_{aliphatic}$), 1600, 1500, 1480 (C=C$_{ar}$). MS (m/z): 861 (M$^+$).

### *9,9′-Diethyl-3,3′-Dicarbazyl-6,6′-Carbaldehyde N,N-Diphenylhydrazone (4b′)*

Was synthesized by the same procedure as **4a**. The yield was 65% of amorphous powder. $^1$H NMR (100 MHz, CDCl$_3$, $\delta$, ppm) 1.50 (t, 6 H,

$2CH_3$), 4.30–4.50 (m, 4 H, $2CH_2$), 7.10–7.35 (m, 12 H, ar), 7.35–7.55 (m, 14 H, ar), 7.80 (d, 2 H, ar), 7.95 (d, 2 H, ar), 8.25 (s, 2 H, ar), 8.4 (s, 2 H, ar). IR (in KBr) $\nu/\mathrm{cm}^{-1}$: 3060 ($C-H_{ar}$), 2980 ($CH_{aliphatic}$), 1600, 1480 ($C{=}C_{ar}$). MS (m/z): 777.3 ($M^+$).

### 9,9′-Diethyl-3,3′-Dicarbazyl-6,6′-Carbaldehyde N-methyl-N-Phenylhydrazone (4b)

Was synthesised by the same procedure as **4a**. The yield was 50% of amorphous powder. $^1$H NMR (100 MHz, $CDCl_3$, $\delta$, ppm) 1.43 (t, 6 H, $2CH_3$), 3.40 (s, 6 H, $2CH_3$), 4.25–4.45 (m, 4 H, $2CH_2$), 6.25–6.95 (m, 2 H, ar), 7.20–7.50 (m, 12 H, ar), 7.65 (s, 2 H, CH), 7.78 (d, 2 H, ar), 7.83 (d, 2 H, ar), 8.40 (s, 4 H, ar). IR (in KBr) $\nu/\mathrm{cm}^{-1}$: 2980, 2900 ($CH_{aliphatic}$), 1600, 1490 ($C{=}C_{ar}$). MS (m/z): 653.2 ($M^+$).

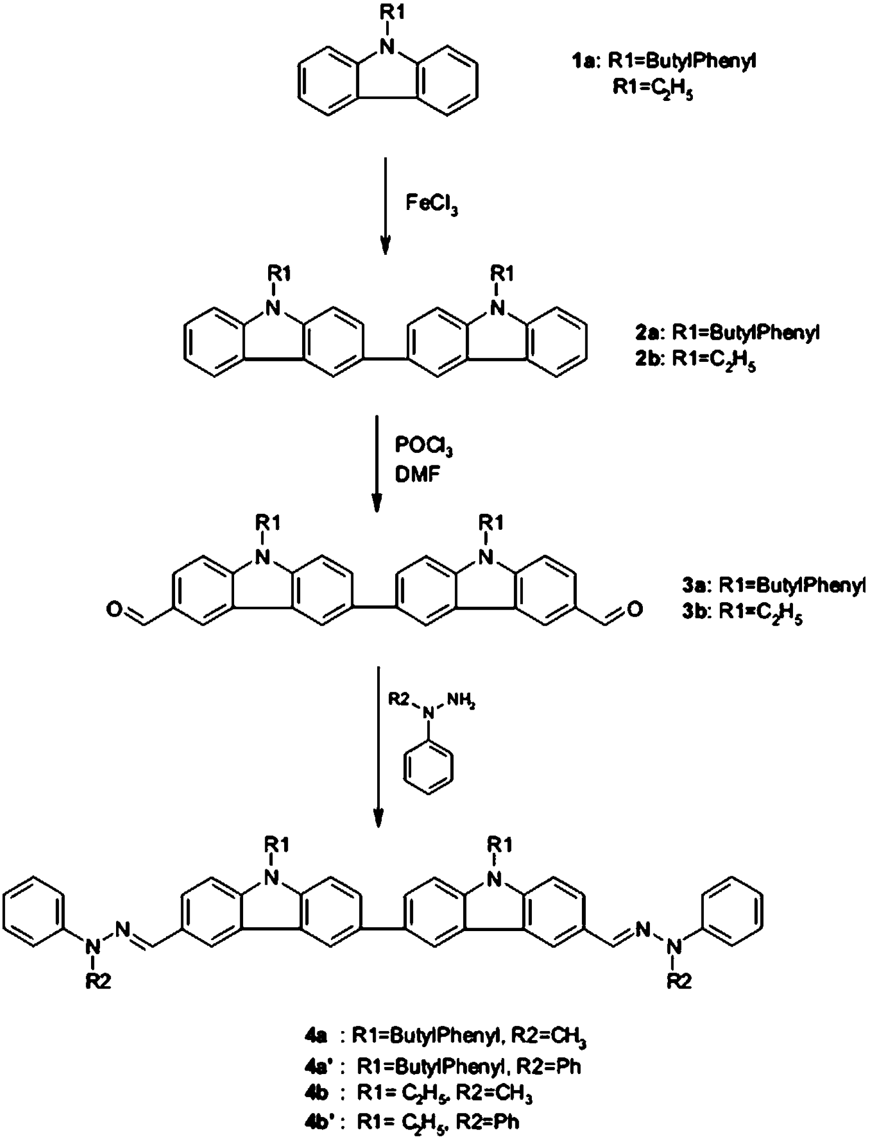
## Methods

$^1$H NMR spectra were obtained on a Bruker AC 250 (250 MHz) and JOEL JNM-FX 100 (100 MHz) instruments. Mass (MS) spectra were obtained on a Waters ZQ (Waters, Milford, USA). IR-spectroscopy was performed on Specord 75 IR and Perkin Elmer Spectrum GX spectrophotometers, using KBr pellets. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 20 instrument, equipped with low temperature probe. Thermogravimetric analysis (TGA) was fulfilled using NETZSCH STA 409 thermogravimeter, at 10°C/min heating rate under $N_2$ atmosphere. UV-VIS spectra were recorded with Spectronic Unicam Genesys™ 8 spectrophotometer. Fluorescence emission spectra were recorded with a Hitachi MPF-4 (Japan) luminescence spectrometer.

The ionisation potential ($I_p$) was measured by the electron photoemission in air method as described before [2]. 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 adhesive layer. Hole drift mobilities were measured by a xerographic time-of-flight method [3].

## RESULTS AND DISCUSSION

We have synthesized N-alkyl and N-alkylphenyl-3,3′ dicarbazylhydrazones by three or four-step synthetic route as shown in Scheme 1. 9-(4-butylphenyl)-9H-carbazole (**1a**) was obtained by an Ullmann coupling reaction of carbazole with an excess of 1-bromo-4-butylbenzene. Oxidative dimerization of **1a** and 9-ethylcarbazole using $FeCl_3$ as a catalyst lead to dimers **2a** and **2b**. The next step was Vilsmeier



**SCHEME 1** Synthetic route to compounds **4a**, **4a**′, **4b** and **4b**′.

formylation of N-substituted carbazole dimers **2a**, **2b** using $POCl_3$/DMF complex to get diformyl compounds **3a**, **3b**. The last step was the condensation of aldehydes **3a** and **3b** with hydrazines having different substituents at a hydrazine N atom. All the final products,

**TABLE 1** Thermal Characteristics of **4a**, **4a′**, **4b** and **4b′**

| Compound | $T_g$ [°C] | $T_o$ [°C][a] |
|---|---|---|
| **4a** | 107 | 291 |
| **4a′** | 99 | 250 |
| **4b** | 133 | 285 |
| **4b′** | — | 272 |

[a] $T_o$ was obtained from the intersection of tangents of vertical and horizontal parts of TG curve.

dihydrazones **4a**, **4a′**, **4b** and **4b′** were purified by the column chromatography to obtain pure and well-defined compounds. The synthesised compounds were characterised by $^1$HNMR, IR spectroscopy and mass spectrometry.

The thermal investigation of 3,3′ -dicarbazyl-based hydrazones was performed by DSC and TGA. The data are presented in Table 1. The temperatures of the onset of the thermal decomposition ($T_o$) of compounds **4a′**and **4b′**, having diphenyl substituted hydrazine N atom, are 250°C and 272°C respectively, while compounds **4a** and **4b**, containing methylphenyl substituted N atom, show the corresponding onset of the thermal decomposition at 291°C and 285°C respectively. It is evident that substituents at hydrazine N atom affect the thermal stability of 3,3′-dicarbazyl-containing hydrazones. The thermal degradation of compounds **4ab** and **4a′ b′** occurs in two stages. The first stage is apparently due to the brake of azo bond of hydrazine moiety. The weight loss percentage of the first step for all hydrazones corresponds to the share of hydrazine moiety in the hydrazone molecules. The second step is a decomposition of the products left after the first step.

Compounds **4ab** and **4a′** exhibit relatively high glass transition temperatures ($T_g$). The highest $T_g$ exceeding 130°C was observed for **4b**. This observation enables to predict high morphological stability for the glass of compound **4b** at the elevated temperatures. The sensitivity of the DSC apparatus used was not sufficient to observe the glass transition of **4b′**. It was only confirmed by DSC that **4b′** was an amorphous compound.

UV-vis spectra of the dilute solutions of the hydrazones synthesized are shown in Figure 1. The band edge of the N,N-diphenylhydrazones (**4a′** and **4b′**) appear to be at 405 nm while N-methyl-N-phenylhydrazones (**4a** and **4b**) band edge appear at 393 nm. The $\pi - \pi^*$ transition maxima of methylphenyl substituted hydrazones are at 348 nm and the maxima of diphenyl substituted hydrazones are batochromically

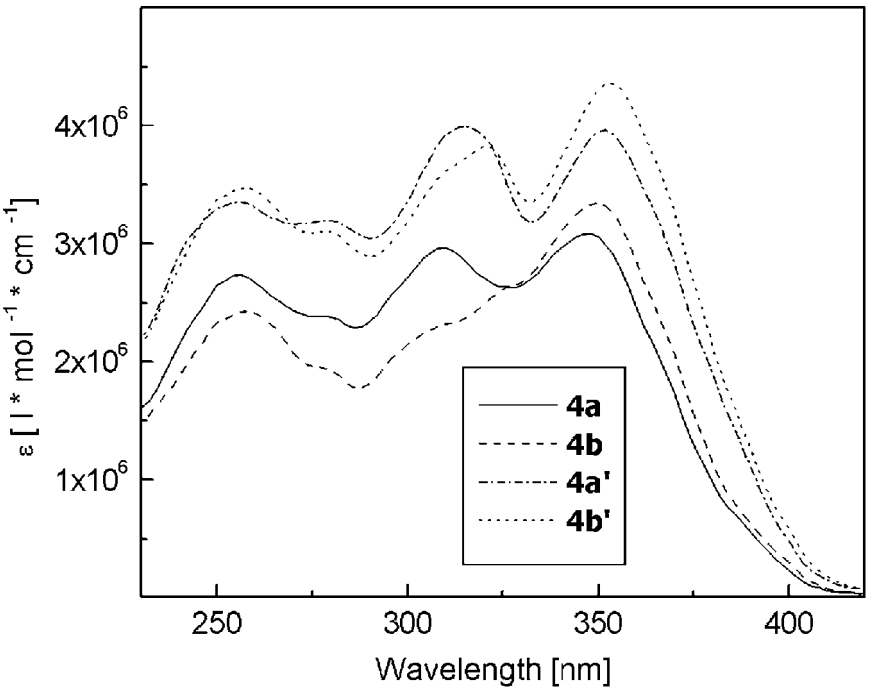


**FIGURE 1** UV-vis absorbtion spectra of dilute THF solutions of **4a**′, **4b**′ and **4a**, **4b**.

shifted by ca. 5 nm (Table 2). Both hyperchromic and batochromic shifts of the lowest energy absorption bands are observed in the spectra of hydrazones **4a**′ and **4b**′ having diphenylsubstituted hydrazine N atoms relative to the spectra of methyl phenyl substituted hydrazones **4a** and **4b**. The substitution at the 9th position of carbazole ring seems to have lower influence to the absorption spectra of

**TABLE 2** Absorption and Emission Maxima of Compounds **4ab** and **4a**′**b**′

| Compound | $\lambda_{\mathrm{abs}}$ [nm][a] | $\lambda_{\mathrm{em}}$ [nm][b] |
|---|---|---|
| **4a** | 348 | 428 |
| **4a**′ | 353 | 432 |
| **4b** | 348 | 423 |
| **4b**′ | 353 | 432 |

[a] The lowest energy absorption band maxima.

[b] Measured in THF solution ($10^{-5}$ mol/l). $\lambda_{\mathrm{ex}} = 350$ nm.

the title hydrazones. All the synthesized hydrazones emit blue-violet light when excited with the ultraviolet light. The emission maxima are given in Table 2.

They range from 423 nm to 432 nm. For the illustration excitation and fluorescence spectra of the dilute solution of **4a′** are given in Figure 2.

Amorphous thin films on the substrate can be prepared by the casting technique from all dicarbazyl hydrazones reported in this presentation. The stabilities of the films with thickness of 0.5–1 μm were sufficient for ionization potential ($I_p$) measurements. The photoemission spectra are presented in Figure 3.

The values of the ionisation potentials, established from the photoemission spectra are presented in Table 3. 9,9′ -(4-butylphenyl)-3,3′-carbazyl-based hydrazones exhibit higher $I_p$ than the corresponding 9-ethyl-substituted compounds. Thus ionization potentials of

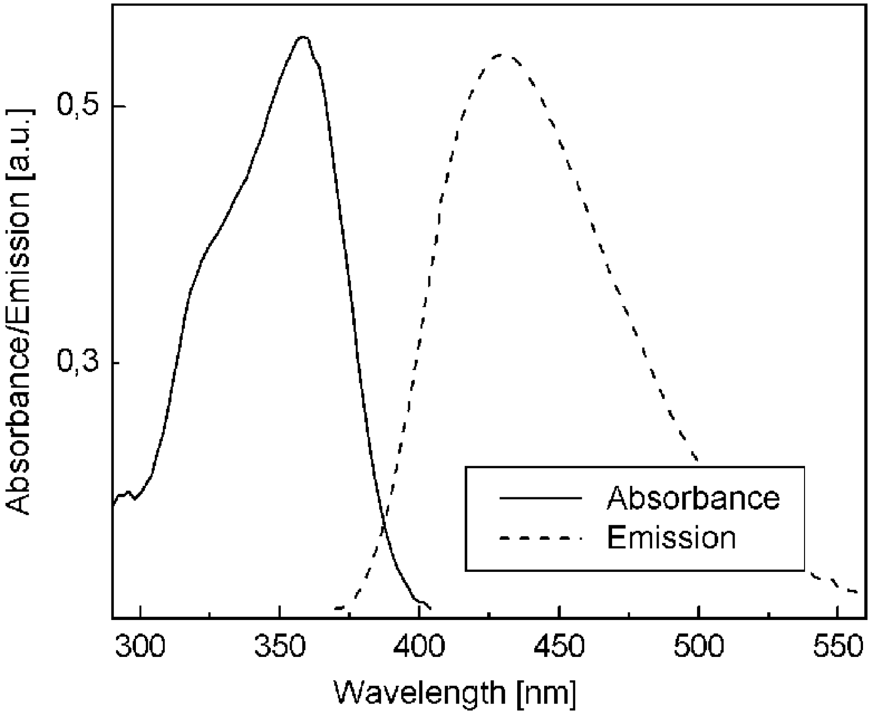


**FIGURE 2** Exitation and emission spectra of **4a′** in THF ($10^{-5}$ mol/l, $\lambda_{ex} = 350$ nm).

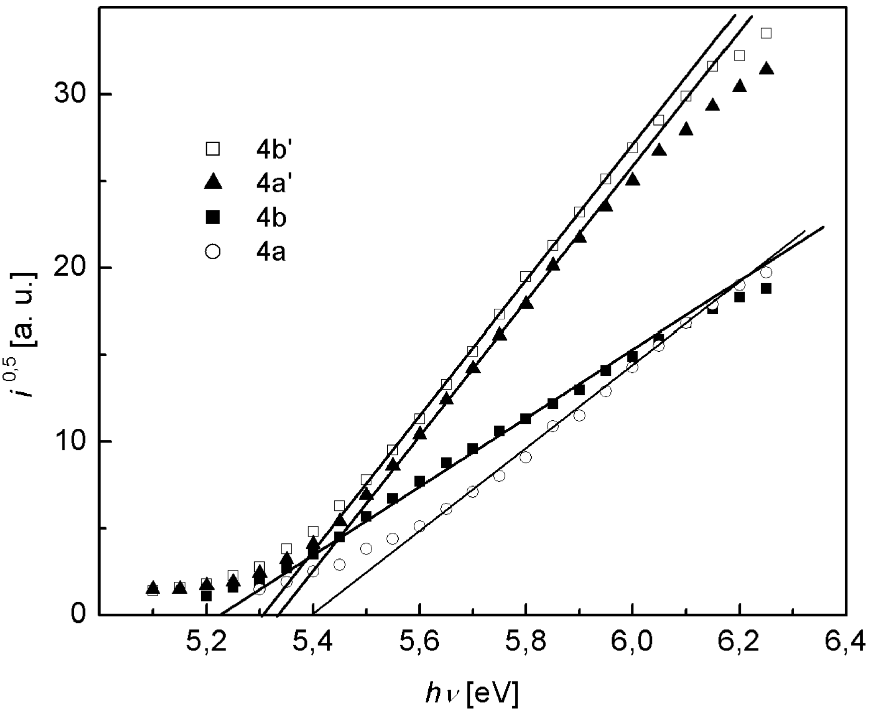


**FIGURE 3** The photoemission spectra of synthesised compounds measured in air at 25°C.

carbazole-based hydrazones can be varied by changing the substituents at the nitrogen atoms.

For the measurements of the hole drift mobilities, amorphous films of 2–10 μm thickness of the pure hydrazones and of their solid solutions in bispenol Z polycarbonate (PC) were prepared. The morphological stability of the glasses of **4a**, **4a**′ allowed the preparation of amorphous films of the pure compounds and of their mixtures with PC. The solubility of compounds **4b**′ and **4b** were insufficient to prepare layers of the necessary thickness for the measurements of the

**TABLE 3** Ionization Potentials of the Films of the 3,3′-Dicarbazyl-Based Hydrazones

| Compound | **4a** | **4a**′ | **4b** | **4b**′ |
|---|---|---|---|---|
| $I_p$, eV | 5,40 | 5,34 | 5,21 | 5,3 |

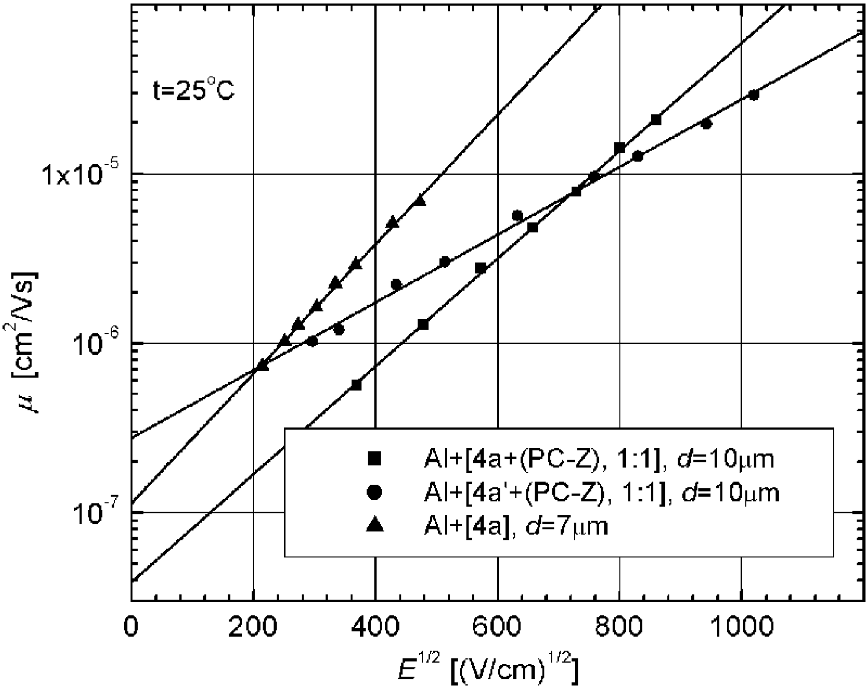


**FIGURE 4** Electric field dependencies of hole drift mobilities of the amorphous film of **4a** and of solid solutions in PC of **4a** and **4a′**, at 25°C.

hole drift mobilities. Figure 4 shows the electric field dependences of the hole drift mobilities of the amorphous films and of the solid solutions in PC of hydrazones **4a** and **4a′**. The hole drift mobility in **4a** could reach $1{,}5 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ at an electric field of $3{,}2 \times 10^5\,\mathrm{V\,cm}^{-1}$, at 25 °C. The hole mobilities of PC doped with **4a′** and **4a** exceed $10^{-6}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ at an electric field of $3{,}2 \times 10^5\,\mathrm{V\,cm}^{-1}$.

## CONCLUSIONS

Synthesis of 3,3′ -dicarbazyl-based hydrazones is reported. The hydrazones form glasses and the amorphous films can be prepared on the substrates by casting from solutions. Glass transition temperatures are in the range of 99°C–133°C. The ionization potentials of the synthesized hydrazones measured by electron photoemission technique range from 5.21 to 5.4 eV. The hole drift mobilities of 3,3′ -dicarbazyl-based hydrazones approach $10^{-5}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ at an electric field of $3{,}2 \times 10^5\,\mathrm{V\,cm}^{-1}$ at 25°C.

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