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High hole mobilities in carbazole-based glass-forming hydrazones

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The properties of a series of carbazole-based dihydrazones are reported. The dependence of their thermal and glass-forming properties on their chemical structure is discussed. The hydrazones having phenyl substituents at the N atom of the hydrazine moiety form glasses and their amorphous films on the glass or polyester substrates can be prepared by casting from solutions. The ionization potentials of the synthesized hydrazones measured by the electron photoemission technique range from 5.24 to 5.50 eV. Hole drift mobilities of some newly synthesized carbazole-based dihydrazones appproach 10^{-2} cm^2 V^{-1} s^{-1} at an electric field of 6.4×10^5 V cm^{-1}, at 22 °C.

Aromatic hydrazones of the general formula RCH=N–NR$_2$, where R are aromatic or heteroaromatic groups, are widely studied as organic hole transport materials.[1–4] Hydrazones as well as aromatic amines, such as *N*,*N*′-diphenyl-*N*,*N*′-bis-(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD)[5] and 1,1-bis(di-4-tolylaminophenyl)cyclohexane (TAPC),[6] 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 holes. 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. Electrophotographic photoreceptors with hydrazone molecules, dispersed in polymer binders, show excellent performance.[7–10] Among the great number of studies devoted to low-molar-mass aromatic hydrazones only a few glass-forming compounds are reported.[11] Carbazole-containing hydrazones described in the literature exhibit relatively high hole drift mobilities.[12,13] Most of carbazole-based hydrazones reported contain only one hydrazine moiety per molecule. Such molecules are rather small and their inclination to crystallize is rather high.[12–14] In this work we report on the properties of carbazole-based dihydrazones. Designing these molecules we expected that an increase of the molar mass of the carbazole-based hydrazones would reinforce the inclination of the molecules to form glasses and the enlarged system of conjugated π-electrons would allow enhanced charge-carrier mobilities. For the comparison of the properties some new carbazole-based monohydrazones have also been synthesized and studied.

Results and discussion

We have synthesized a series of 9-alkyl- and 9-phenylcarbazolylhydrazones by two-step reaction, as schematically shown in Fig. 1. The first step was the formylation of 9-substituted carbazoles **1a–c** using the Vilsmeier reaction[15] to get mono- and diformyl compounds **2a–c**′. The second step was condensation of aldehydes **2a–c**′ with differently substituted hydrazines. All final products, hydrazones **3a–c**′ and **4a–c**′, were purified by column chromatography. After column chromatography all the hydrazones except **3c**′ and **4c**′ were recrystallized from ethanol or methanol to obtain pure and well defined compounds. Compounds **3c**′ and **4c**′ were isolated as amorphous powders after column chromatography. All carbazole-based hydrazones were characterized by IR, ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis (see Experimental section). They are soluble in common organic solvents such as chloroform, acetone, and THF.

The thermal properties of 9-alkyl- and 9-phenylcarbazolylhydrazones were examined by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. The data from the TG investigations of the selected samples are presented in Table 1. These data show the relatively high thermal stability of all the molecules synthesized. A 5% weight loss for compounds **3a**, **3c**, **4a** and **4b**, having diphenyl substituted hydrazine N atoms, is observed at 260 °C, while compounds **4a**′ and **4b**′, containing a methylphenyl substituted N atom, show a corresponding weight loss at 290 °C. The 5% weight loss temperature ($T_{\mathrm{dec}\,-\,5\%}$) for carbazole-based monohydrazones **3a,c** is the same as for dihydrazones **4a,b**, *i.e.* 260 °C. It is evident, that the substituents at the hydrazine N atom affect the 5% weight loss temperature and consequently the thermal stability of the carbazole-containing hydrazone compounds. Neither the introduction of the second hydrazine moiety into the molecule nor a change of the substituent at the carbazole N atom influence the 5% weight loss temperature of the hydrazone compounds synthesized. This observation indirectly shows that the thermal degradation of these compounds starts from the hydrazone group.

Two stages are characteristic of the thermal degradation of the carbazolylhydrazones synthesized. As an illustration of this the TG curves of the hydrazones having different substituents at the hydrazine N atom (**4a** and **4a**′) are shown in Fig. 2. The first step is apparently due to breaking of the azo bond of the hydrazine moiety. The weight loss percentage in this stage for all hydrazones corresponds to the share of hydrazine moiety in the hydrazone molecules. The onset of the second step for

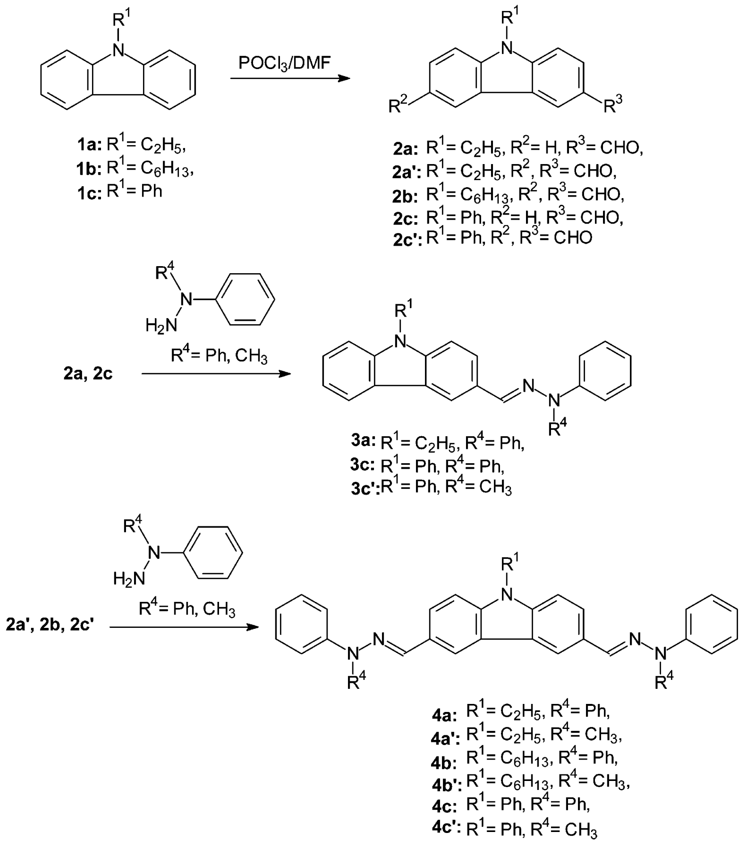

Fig. 1 Scheme of the synthesis of the 9-substituted carbazolylhydrazones.

Table 1 TG data for selected 9-substituted carbazolylhydrazones

Compound	**3a**	**3c**	**4a**	**4a′**	**4b**	**4b′**
$T_{\mathrm{dec}-5\%}$/°C	260	260	260	290	260	290

hydrazones **4a** and **4a′** is observed at approximately the same temperature while the 5% weight loss temperature differs by 30 °C.

The temperatures of the thermal transitions of the selected hydrazones are summarized in Table 2. 9-Alkylcarbazole-based hydrazones having methyl substituents at the hydrazine N atom (**4a′** and **4b′**) are more inclined to crystallization than the corresponding diphenyl substituted hydrazones (**4a** and **4b**).

The compounds with diphenyl substituted hydrazine N atoms (**4a** and **4b**) neither melt nor crystallize in the second heating run of the DSC experiment, however hydrazones having methyl substituents show crystallization and a following melting in the second DSC heating run. An illustration of the DSC thermograms of carbazolylhydrazones having different substituents at the hydrazine N atom (**4a** and **4a′**) is presented in Fig. 3. The first DSC run of diphenyl-substituted hydrazone **4a** reveals melting at 200 °C but after slow cooling the second heating run reveals only a glass transition at 88 °C. Methylphenyl-substituted hydrazone **4a′** melts at 236 °C as is shown by the DSC curve of the first heating run. The DSC curve of **4a′** obtained in the second heating run shows not only a glass transition at 79 °C but also crystallization at 133 °C and then melting at 232 °C. 9-Phenylcarbazole-based hydrazones seem to be more inclined to form glasses than 9-alkylcarbazole-based hydrazones. The DSC curves of **4c′** and **4c** obtained after heating the samples to the melt and slow cooling do not show any crystallization peaks. Apparently the incorporation of the rigid phenyl group into the molecules hinders the packing of molecules and increases the stability of the amorphous state. Incorporation of the phenyl group also markedly increases the T_g of the compounds (see Table 2). Thus the T_g of compound **4c** is by 25 °C higher than that of compound **4b** although the

Table 2 DSC data for the 9-substituted carbazolylhydrazones

Compound	T_g/°C	T_m/°C	T_{cr}/°C
3a	55	161[a]	—
3c	51	214	175
4a	88	200[a]	—
4a′	79	232	133
4b	64	135[a]	—
4b′	45	207	101
4c	89	252[a]	—
4c′	91	—	—

[a] 1st heating only.

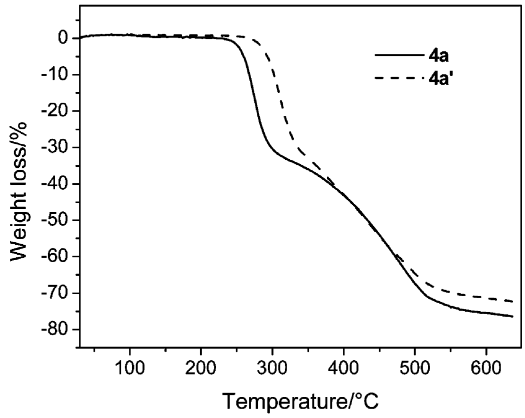

Fig. 2 TG curves of hydrazones **4a** and **4a′** at a heating rate of 10 K min^{-1}, N_2 atmosphere.

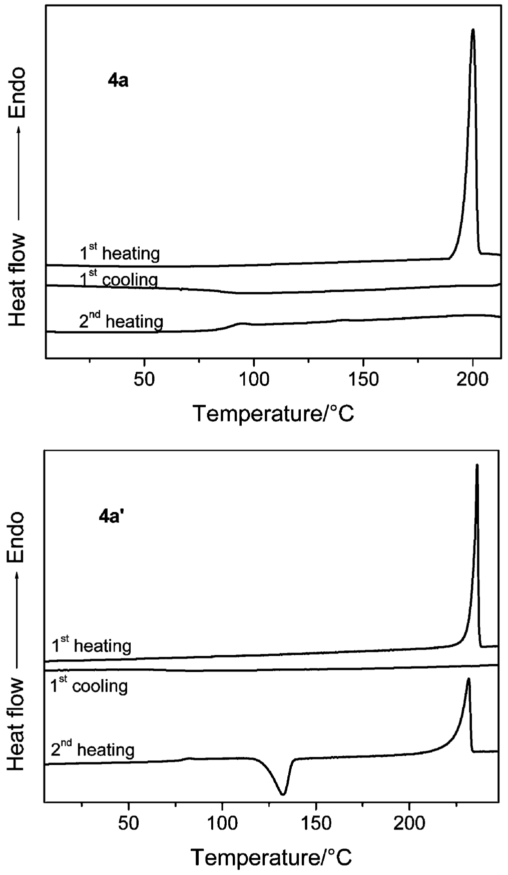

Fig. 3 DSC curves of hydrazones **4a** and **4a′** at a heating rate of 10 K min^{-1}, N_2 atmosphere.

molar masses of these compounds are very similar. The comparison of the values of T_g of *N*,*N*-diphenyl-substituted hydrazones (**4a**, **4b**) and *N*-methyl-*N*-phenyl-substituted hydrazones (**4a′**, **4b′**) reveals a similar effect. The T_g's of the disubstituted carbazolylhydrazones (**4a**, **4c**) are markedly higher than those of their monosubstituted counterparts (**3a**, **3c**).

The synthesized hydrazones absorb light in the 240–450 nm region. As an example, the UV–vis absorption spectra of hydrazones **4a**, **4a′** are shown in Fig. 4. For a comparison the spectrum of 9-ethyl-9*H*-carbazole is given in Fig. 4. The spectra of the hydrazones **4a**, **4a′** exhibit a strong bathochromic shift with respect to the spectrum of 9-ethyl-9*H*-carbazole. In the UV spectra of the hydrazones, B and R bands are submerged by the bathochromically and hyperchromically shifted K bands attributed to π→π* transitions.[16] This observation shows that the molecules of the dihydrazones are strongly π-conjugated through the lone electron pairs of the nitrogen atoms and that the π-electrons are delocalized in these molecules.

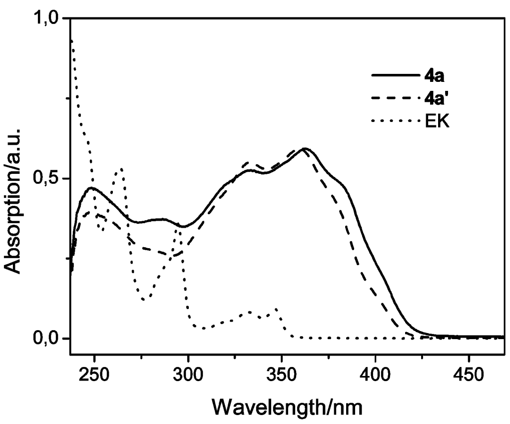

Fig. 4 UV–vis absorption spectra ($CHCl_3$ solutions) of hydrazones **4a** and **4a′**, and 9-ethyl-9*H*-carbazole.

Amorphous thin films on the substrate of different morphological stability can be prepared by the casting technique from all carbazolyl hydrazones reported in this presentation. The stabilities of the films with thicknesses of 0.5–1 μm were sufficient for ionization potential (I_p) measurements. The values of I_p are given in Table 3. The I_p of the dihydrazones **4a** and **4b**, having a diphenyl-substituted N atom of the hydrazine moiety, is by about 0.1 eV higher than the I_p of dihydrazones **4a′** and **4b′**, which bear a methyl substituent at the hydrazine N atom. The 9-phenyl-9*H*-carbazolyl-based hydrazones exhibit higher I_p than the 9-alkyl-substituted compounds. Thus ionization potentials of carbazole-based hydrazones can be varied by changing the substituents at the nitrogen atoms.

For the measurements of the electrophotographic parameters and hole drift mobilities, amorphous films of 2–10 μm thickness of the pure hydrazones or of their solid solutions in polycarbonate (PC) were prepared. The morphological stability of the glasses of **3c′**, **4a**, **4b** and **4c′** allowed the preparation of amorphous films of the pure compounds and of their mixtures with PC. The solubility of compound **4a′** was insufficient to prepare layers of the necessary thickness. The morphological stability of the glasses of hydrazones **3c**, **4c**, **4b′** was not high enough to prepare amorphous films of the pure compounds and the measurements of the electrohotographic parameters and hole mobilities were carried out using their solid solutions in PC.

The electrophotographic parameters of the films of carbazolylhydrazones and/or of their solid solutions in PC are presented in Table 4.

The photosensivity ($S_{1/2}$) of the carbazolylhydrazones reported in this presentation is similar to that of known compounds having carbazole moieties.[17] It decreases several times after the introduction of 50 wt.% PC. Nevertheless it is high enough for hole drift mobility measurements. The low U_R/U_0 ratio shows that the large majority of holes generated at the surface of the layers traverse through their volume and reach the opposite side. This observation shows that hole transport is effective in these materials.

The results of the time-of-flight measurements corroborate the data from the electrophotographic research. Fig. 5 shows the electric field dependences of the hole drift mobilities of the

Table 3 Ionization potentials of the films of the 9-substituted carbazolylhydrazones

Compound	3a	3c	3c′	4a	4a′	4b	4b′	4c	4c′
I_p/eV	5.40	5.47	5.47	5.35	5.27	5.37	5.24	5.46	5.50

Table 4 Electrophotographic parameters of the 9-substituted carbazolylhydrazones (steady light 10^{17} quanta s^{-1} m^{-2}, λ = 295 nm, 20 °C)

Compound	*d*/μm	U_0/V	U_R/V	U_R/U_0	$S_{1/2}$/m^2 J^{-1}
3c+ PC	8.3	798	72	0.089	0.45
3c′	6.3	428	56	0.028	3.0
3c′ + PC	3.8	500	18	0.036	0.56
4a	4.5	229	3.9	0.017	6.9
4b	3.6	336	6	0.0018	7.9
4b′+ PC	3.6	372	16	0.043	2.7
4c	8.5	200	12	0.06	2.7
4c+ PC	3.2	248	10	0.04	1.7
4c′	4.5	408	8	0.02	7.7
4c′+ PC	3.8	436	10	0.023	1.7

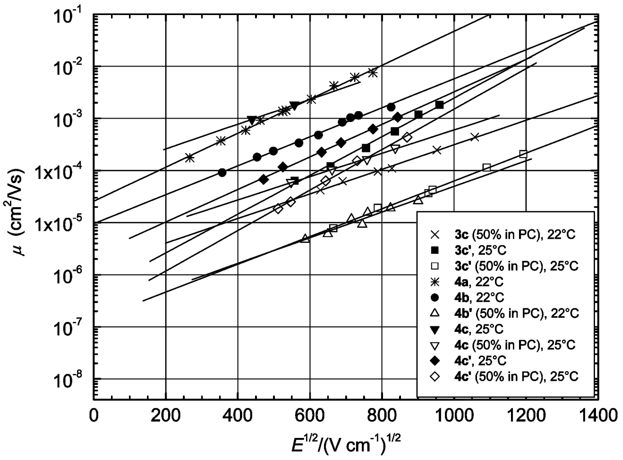

Fig. 5 Electric field dependence of the hole drift mobility of the amorphous films of the 9-substituted carbazolylhydrazones and their solid solutions in PC, at 22–25 °C.

amorphous films of hydrazones **3c**′, **4a**, **4b**, **4c** and **4c**′ and of the solid solutions in PC of **3c**, **3c**′, **4b**′, **4c** and **4c**′. The highest hole drift mobilities were observed in glasses **4a**, **4b** and **4c**. The hole drift mobility in **4a** reaches 10^{-2} cm^2 V^{-1} s^{-1} at an electric field of 6.4 × 10^5 V cm^{-1}, at 22 °C. To our knowledge this is one of the highest charge mobilities in disordered organic solids reported up to now. The dihydrazone **4b**, with a longer alkyl substituent, exhibits a little lower hole drift mobility than those of hydrazones **4a** and **4c**, apparently due to the lower concentration of the functional units. Hydrazones containing two hydrazine moieties per molecule (**4a**, **4c** and **4c**′) show higher hole drift mobilities than mono-substituted hydrazones **3a**, **3c** and **3c**′. This is apparently due to the larger systems of conjugated π-electrons in **4c** and **4c**′. A similar reason apparently predetermines the higher hole drift mobility in **4c** relative to **4c**′. The hole mobilities of PC doped with **4c** and **4c**′ markedly exceed 10^{-4} cm^2 V^{-1} s^{-1} at an electric field of 6.4 × 10^5 V cm^{-1}. These are also very high charge mobilities, as for molecularly doped polymer.

Conclusions

A series of carbazole-based dihydrazones were synthesized. The hydrazones having phenyl substituents at the N atom of the hydrazine moiety form glasses and amorphous films of them can be prepared on the substrates by casting from solutions. The ionization potentials of the synthesized hydrazones measured by electron photoemission range from 5.24 to 5.50 eV. The hole drift mobilities of some carbazole-based dihydrazones appproach 10^{-2} cm^2 V^{-1} s^{-1} at an electric field of 6.4 × 10^5 V cm^{-1}, at 22 °C.

Experimental

Materials

The starting compounds: 9-ethyl-9*H*-carbazole (**1a**), 9-phenyl-9*H*-carbazole (**1c**), 9-ethyl-9*H*-carbazole-3-carbaldehyde (**2a**), and all the required chemicals: 9*H*-carbazole, 1-bromohexane, potassium hydroxide, tetrabutylammonium hydrosulfate, phosphorus oxychloride, sodium acetate, *N*,*N*-diphenylhydrazine chloride and *N*-methyl-*N*-phenylhydrazine were purchased from Aldrich and purified using standard procedures. Organic solvents were purified and dried as usual. Silica gel was used for column chromatography.

N-hexylcarbazole (**1b**) was synthesized as described in the literature.[18] 1–2 g of mono- and diformyl compounds **2a**′–**c**′ were synthesized by the Vilsmeier reaction of *N*-substituted carbazoles **1a–c** with $POCl_3$ by the following general procedure.

$POCl_3$ (1 equiv) was added dropwise to dry dimethylformamide (1.2 equiv) at 0 °C under an N_2 atmosphere. The solution (*ca.* 2 wt.%) of carbazole derivatives in dry *o*-dichlorobenzene was added stepwise during *ca.* 15 min to the reaction flask. The reaction mixture was stirred at 85 °C until the starting compound was reacted (TLC monitoring). Then the reaction mixture was cooled to room temperature, poured in to ice water and neutralized with sodium acetate to pH = 6–8. The aqueous solution was extracted with chloroform several times. The chloroform solution was washed with water, dried with anhydrous sodium sulfate, filtered and the solvent removed. The crude product was purified by column chromatography (silica gel, eluent: acetone–hexane, 1 : 3).

9-Ethyl-9*H*-carbazole-3,6-dicarbaldehyde (2a′). Yield 78%, ($C_{16}H_{13}NO_2$ = 251.3 g mol^{-1}). IR (KBr), $\bar{\nu}$/cm^{-1}: 1684 (CHO), 1598, 1489 (ar. C=C). MS (*m*/*z*): 251 (M$^+$), 236, 222, 207, 178. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.53 (t, 3H, alk.), 4.45 (m, 2H, alk.), 7.53 (d, 2H, ar.), 8.07 (d, 2H, ar.), 8.63 (s, 2H, ar.), 10.12 (s, 2H, CHO). Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57, Found: C, 76.61; H, 5.30; N, 5.43%.

9-Hexyl-9*H*-carbazole-3,6-dicarbaldehyde (2b). Yield 35%, ($C_{20}H_{21}NO_2$ = 307.5 g mol^{-1}). IR (KBr), $\bar{\nu}$/cm^{-1}: 2953, 2858 (alk. C–H), 1685 (CHO), 1593, 1487 (ar. C=C). MS (*m*/*z*): 307 (M$^+$), 279, 263, 248, 236, 220. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.85 (t, 3H, alk.), 1.30 (m, 6H, alk.), 1.88 (m, 2H, alk.), 4.48 (t, 2H, alk.), 7.52 (d, 2H, ar.), 8.08 (d, 2H, ar.), 8.63 (d, 2H, ar.), 10.10 (s, 2H, CHO). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: 78.29; H, 7.02; N, 4.62%.

9-Phenyl-9*H*-carbazole-3-carbaldehyde (2c). Yield 51%, ($C_{19}H_{13}NO$ = 271.3 g mol^{-1}). IR (KBr), $\bar{\nu}$/cm^{-1}: 3060 (ar. C–H), 1700 (CHO), 1600, 1500 (ar. C=C), 1280 (C–N). MS (*m*/*z*): 271 (M$^+$), 242. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.30–7.75 (m, 9H, ar.), 7.93 (d, 1H, ar.), 8.20 (d, 1H, ar.), 8.65 (s, 1H, ar.), 10.12 (s, 1H, CHO). Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.34; H, 4.98; N, 5.24%.

9-Phenyl-9*H*-carbazole-3,6-dicarbaldehyde (2c′). Yield 43%, ($C_{20}H_{13}NO_2$ = 299.3 g mol^{-1}). IR (KBr), $\bar{\nu}$/cm^{-1}: 3080 (ar. C–H), 1700 (CHO), 1600, 1500 (ar. C=C), 1290 (C–N). MS (*m*/*z*): 299 (M$^+$), 269, 240. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.30–7.75 (m, 7H, ar.), 8.03 (d, 2H, ar.), 8.70 (s, 2H, ar.), 10.15 (s, 2H, CHO). Anal. Calcd for $C_{20}H_{13}NO_2$: C, 80,25; H, 4.38; N, 4.68. Found: C, 80.40; H, 4.45; N, 4.74%.

1–2 g of hydrazones **3a–c**′ and **4a–c**′ were prepared by condensation of aldehydes **2a–c**′ and the derivatives of hydrazine by the following general procedure.

A solution of *N*,*N*-diphenylhydrazine hydrochloride (or *N*-methyl-*N*-phenylhydrazine) in ethanol or methanol was added dropwise to a solution of mono- or diformyl compound in ethanol or methanol by stirring. Molar ratio, 2 mol of hydrazine : 1 formyl group. The reaction mixture was refluxed until all aldehyde was reacted (TLC monitoring). Then the reaction mixture was cooled to the room temperature. The precipitated product was filtered and purified by column chromatography (silica gel, eluent chloroform–hexane, 1 : 2). followed by recrystallization from ethanol or methanol. Compounds **3c**′ and **4c**′ was isolated as amorphous powders after column chromatography.

9-Ethyl-9*H*-carbazole-3-carbaldehyde *N*,*N*-diphenylhydrazone (3a). Yield 43%, ($C_{27}H_{23}N_3$ = 389.5 g mol^{-1}), mp 160–161 °C. IR (KBr), $\bar{\nu}$/cm^{-1}: 3050 (ar.C–H), 2970, 2925 (alk. C–H), 1630 (C=N), 1598, 1500 (ar. C=C), 1300 (C–N). MS (*m*/*z*): 389 (M$^+$), 360, 283, 205, 194, 179 168, 165, 77. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.41 (t, 3H, alk.), 4.33 (m, 2H, alk.), 7.10–7.50 (m, 15H, ar.), 7.85 (d, 1H, ar.), 8.05 (d, 1H, ar.), 8.20 (s, 1H, methine). Anal. Calcd for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.79. Found: C, 83.48; H, 6.04; N, 10.93%.

9-Phenyl-9*H*-carbazole-3-carbaldehyde *N*,*N*-diphenylhydrazone (3c). Yield 77%, ($C_{31}H_{23}N_3$ = 437.5 g mol^{-1}), mp 213–214 °C. IR (KBr), $\bar{\nu}$/cm^{-1}: 3060 (ar. C–H), 1630 (C=N), 1600, 1500 (ar. C=C), 1300 (C–N). MS (*m*/*z*): 437 (M$^+$), 360, 268, 241, 168. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.10–7.30 (m, 7H, ar.), 7.30–7.50 (m, 9H, ar.), 7.50–7.70 (m, 4H, ar.), 7.83 (d, 1H, ar.), 8.13 (d, 1H, ar.), 8.25 (s, 1H, methine). Anal. Calcd for $C_{31}H_{23}N_3$: C, 85.10; H, 5.30; N, 9.60. Found: C, 85.41; H, 5.41; N, 9.75%.

9-Phenyl-9*H*-carbazole-3-carbaldehyde *N*-methyl-*N*-phenylhydrazone (3c′). Yield 83 %, ($C_{26}H_{21}N_3$ = 375.5 g mol^{-1}). IR (KBr) $\bar{\nu}$/cm^{-1}: 3050 (ar. C–H), 2940 (alk. C–H), 1630 (C=N), 1600, 1500 (ar. C=C), 1300 (C–N). MS (*m*/*z*): 375 (M$^+$), 284, 269. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.50 (s, 3H, methyl), 6.93 (t, 1H, ar.), 7.20–7.50 (m, 11H, ar.), 7.50–7.65 (m, 2H, ar.), 7.75 (s, 1H, ar.), 7.85 (d, 1H, ar.), 8.20 (d, 1H, ar.), 8.40 (s, 1H, methine). Anal. Calcd for $C_{26}H_{21}N_3$: C, 83.17; H, 5.64; N, 11.19. Found: C, 83.60; H, 5.71; N, 11.37%.

9-Ethyl-9*H*-carbazole-3,6-dicarbaldehyde bis(*N*,*N*-diphenylhydrazone) (4a). Yield 91%, ($C_{40}H_{33}N_5$ = 583,7 g mol^{-1}), 199.5–200.5 °C. IR (KBr), $\bar{\nu}$/cm^{-1}: 3059 (ar. C–H), 2975, 2931 (alk. C–H), 1629 (C=N), 1590, 1494 (ar. C=C), 1293 (C–N). MS (*m*/*z*): 583 (M$^+$), 428, 414, 388, 359, 246, ,204, 168, 77. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.38 (t, 3H, alk.), 4.31 (m, 2H, alk.), 7.16–7.46 (m, 24H, ar.), 7.83 (d, 2H, ar.), 8.20 (s, 2H, methine). Anal. Calcd for $C_{40}H_{33}N_5$: C, 82.30; H, 5.70; N, 12.00. Found: 83.14; H, 5.69; N, 12.21%.

9-Ethyl-9*H*-carbazole-3,6-dicarbaldehyde bis(*N*-methyl-*N*-phenylhydrazone) (4a′). Yield 35%, ($C_{30}H_{29}N_5$ = 459.6 g mol^{-1}), mp 229–230.5 °C. IR (KBr), $\bar{\nu}$/cm^{-1}: 3052 (ar. C–H), 2973, 2930, 2893 (alk. C–H), 1629 (C=N), 1593, 1500 (ar. C=C), 1296 (C–N). MS (*m*/*z*): 459 (M$^+$), 430, 352, 326, 296, 230, 164, 133, 106, 77. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.45 (m, 3H, alk.), 3.45 (d, 6H, methyl), 4.35 (m, 2H, alk.), 6.90 (m, 2H, ar.), 7.26–7.48 (m, 10H, ar.), 7.70 (d, 2H, ar.), 7.90 (m, 2H, ar.), 8.40 (d, 2H, methine). Anal. Calcd for $C_{30}H_{29}N_5$: C, 78.40; H, 6.36; N, 15.24. Found: C, 78.91; H, 6.47; N, 15.43%.

9-Hexyl-9*H*-carbazole-3,6-dicarbaldehyde bis(*N*,*N*-diphenylhydrazone) (4b). Yield 53%, ($C_{44}H_{41}N_5$ = 639,8 g mol^{-1}), mp 134–135 °C. IR (KBr), $\bar{\nu}$/cm^{-1}: 3059, 3035 (ar. C–H), 2953, 2926, 2856 (alk. C–H), 1628 (C=N), 1590, 1494 (ar. C=C), 1292 (C–N). MS (*m*/*z*): 637, 563, 470, 397, 317, 275, 168, 77. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.84 (t, 3H, alk.), 1.29 (m, 6H, alk.), 1.83 (m, 2H, alk.), 4.24 (m, 2H, alk.), 7.16–7.46 (m, 2H, ar.), 7.85 (d, 2H, ar.), 8.20 (s, 2H, methine). Anal. Calcd for $C_{44}H_{41}N_5$: C, 82.59; H, 6.46; N, 10.59; Found: C, 82.94; H, 6.61; N, 10.78%.

9-Hexyl-9*H*-carbazole-3,6-dicarbaldehyde bis(*N*-methyl-*N*-phenylhydrazone) (4b′). Yield 84%, ($C_{34}H_{37}N_5$ = 515.7 g mol^{-1}), mp 203–205 °C. IR (KBr), $\bar{\nu}$/cm^{-1}: 3055 (ar. C–H), 2953, 2925, 2856 (alk. C–H), 1629 (C=N), 1595, 1500 (ar. C=C), 1293 (C–N). MS (*m*/*z*): 515 (M$^+$), 444, 408, 382, 323, 258, 204, 178, 164, 77. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.85 (s, 3H, alk.), 1.30 (s, 6H, alk.), 1.85 (s, 2H, alk.), 3.45 (s, 6H, methyl), 4.36 (s, 2H, alk.), 6.92 (d, 2H, ar.), 7.26–7.49 (m, 10H, ar.), 7.72 (s, 2H, ar.), 7.90 (d, 2H, ar.), 8.35 (s, 2H, methine). Anal. Calcd for $C_{34}H_{37}N_5$: C, 79.18; H, 7.23; N, 13.58. Found: 79.41; H, 7.34; N, 13.71%.

9-Phenyl-9*H*-carbazole-3,6-dicarbaldehyde bis(*N*,*N*-diphenylhydrazone) (4c). Yield 72 %, ($C_{44}H_{33}N_5$ = 631.8 g mol^{-1}), mp 250–252 °C. IR (KBr), $\bar{\nu}$/cm^{-1}: 3050 (ar. C–H), 1590, 1480 (ar. C=C), 1300 (C–N). MS (*m*/*z*): 631 (M$^+$), 464, 268, 242. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.15–7.65 (m, 27H, ar.), 7.70–7.80 (m, 4H, ar.), 8.30 (s, 2H, methine). Anal. Calcd for $C_{44}H_{33}N_5$: C, 83.65; H, 5.26; N, 11.09. Found: C, 83.94; H, 5.34; N, 11.12%.

9-Phenyl-9*H*-carbazole-3,6-dicarbaldehyde bis(*N*-methyl-*N*-phenylhydrazone) (4c′). Yield 68%, ($C_{34}H_{30}N_5$ = 508.6 g mol^{-1}) of amorphous powder. IR (KBr), $\bar{\nu}$/cm^{-1}: 3050 (ar. C–H), 2910 (alk. C–H), 1590, 1490 (ar. C=C), 1295 (C–N). MS (*m*/*z*): 508 (M$^+$), 402, 242. ^{1}H NMR ($CDCl_3$), δ (ppm): 3.50 (s, 6H, methyl), 6.95 (t, 2H, ar.), 7.30–7.50 (m, 11H, ar.), 7.55–7.70 (m, 4H, ar.), 7.75 (s, 2H, ar.), 7.85 (d, 2H, ar.), 8.45 (s, 2H, methine). Anal. Calcd for $C_{34}H_{30}N_5$: C, 80.28; H, 5.94; N, 13.77. Found: C, 80.64; H, 6.05; N, 13.94%.

Instrumentation

Nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker AC 250 (250 Hz). IR and UV–vis absorption spectra were recorded using a Bio-Rad Digilab FTS-40 and UV–vis Hitachi U-3000 spectrophotometer, respectively. Electron impact mass spectra were obtained on a Finnigan MAT 8500 (70 eV) with a MAT 112 S, Varian. DSC measurements were carried out with a PerkinElmer DSC-7 at 10 K min^{-1} heating rate under N_2 atmosphere. TG analysis was performed on a Netzsch STA 409 with data acquisition system 414/1, at a 10 K min^{-1} heating rate, under an N_2 atmosphere.

Sample preparation

The samples for the ionization potential measurements were prepared by casting films from THF solutions on Al plates, pre-coated with ∼0.5 µm thick methylmethacrylate and a methacrylic acid copolymer (MKM) adhesive layer. A 0.3% solution of MKM in a 1 : 1 acetone–water mixture was used for pre-coating. The function of this layer was not only to improve adhesion, but also to eliminate the electron photoemission from the Al layer. No photoemission was detected from the Al layer over-coated with MKM at illumination with up to 6.25 eV quanta energy light. In addition, the MKM layer is conductive enough to avoid charge accumulation on it during measurements. The thickness of the film of hydrazone compound was 0.5–1 µm. The ionization potentials were measured by the electron photoemission in air method.[19,20]

The films for the measurements of the charge carrier mobility were prepared by casting from 10–12% THF solutions of the hydrazone compounds or their mixtures with PC at a mass proportion of 1 : 1. The substrates were glass plates with a conductive SnO_2 layer or polyester film with an Al layer. After preparation, the samples were dried at 80 °C for 1 h. The thickness of the charge transporting layers varied in the range of 2–10 µm.

Hole drift mobility measurements

The hole drift mobility was measured by a time-of-flight method[21] in an electrophotographic regime.[22] The electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses from a nitrogen laser (pulse duration was 2 ns, λ = 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of the initial potential before illumination. A capacitance probe connected to the wide frequency band electrometer was used to measure the rate of the surface potential decrease d$U\cdot$dt^{-1} The transit time t_t for was determined by the kink on the curve of the d$U\cdot$dt^{-1} transient on the linear or double logarithm plot. The drift mobility was calculated by the formula $\mu = d^2\cdot U_0{}^{-1}\cdot t_t{}^{-1}$, where d is the layer thickness, andd U_0 is the surface potential at the moment of illumination.

Measurements of electrographic parameters

The electrographic parameters of the layers were measured using standard electrographic research procedures.[23] The photosensivity ($S_{1/2}$/m^2 J^{-1}) was defined using the half value of the initial potential criteria. For this measurement the layers were illuminated with light of the constant intensity (10^{17} quanta s^{-1} m^{-2}). The residual potential (U_R) was measured after illumination of a layer with $(U_0(\mathrm{d}U\cdot\mathrm{d}t^{-1})_0{}^{-1})$ 10^{18} quanta s^{-1} m^{-2} units of light (U_0 is the initial potential, $(\mathrm{d}U\cdot\mathrm{d}t^{-1})_0$ is the initial rate of potential photodecay) at a low rate of surface potential decay.

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References

1 P. Strohriegl and J. V. Grazulevicius, in *Advanced Functional Molecules and Polymers*, ed. H. S. Nalwa, Gordon & Breach, Chichester, 2001, vol. 3, p. 1–77.
2 P. M. Borsenberger, *Adv. Mater. Opt. Electron.*, 1992, **1**, 73–80.
3 S. Nomura, K. Nishimura and Y. Shirota, *Thin Solid Films*, 1996, **273**, 27–34.
4 S. Nomura, K. Nishimura and Y. Shirota, *Mol. Cryst. Liq. Cryst.*, 1998, **313**, 247–252.
5 C. H. Chen, J. Shi and C. W. Tang, *Macromol. Symp.*, 1998, **125**, 1–48.
6 P. M. Borsenberger, L. Pautmeier, R. Richert and H. Bässler, *J. Chem. Phys.*, 1991, **94**, 8276–8281.
7 N. Mori, *US Pat.*, 5 567 557, 1996, CAS No 123:241957.
8 N. Tatsya and U. Minoru, *Jpn. Pat.*, 8 101 524, 1996, CAS No125:100121.
9 V. Gaidelis, J. Gavutiene, V. Getautis, J. V. Grazulevicius, V. Jankauskas, R. Kavaliunas, R. Lazauskaite, O. Paliulis, M. Rossman, D. J. Sidaravicius, T. S. Smith and A. Stanishauskaite, *US Pat.*, 6 214 503, 2001, CAS No 134:273544.
10 Y. Suzuki, *US pat.*, 5 665 500, 1997, CAS No 125:22263.
11 H. Nam, D. H. Kang, J. K. Kim and S. Y. Park, *Chem. Lett.*, 2000, **11**, 1298–1299.
12 S. Nomura, K. Nishimura and Y. Shirota, *Mol. Cryst. Liq. Cryst.*, 1998, **315**, 519–524.
13 A. Fujii, T. Shoda, S. Aramaki and T. Murayama, *J. Imaging Sci. Technol.*, 1999, **43**, 430–436.
14 K. Naito and A. Miura, *J. Phys. Chem.*, 1993, **97**, 6240–6248.
15 A. Vilsmeier and A. Haack, *Ber.*, 1927, **60**, 119–122.
16 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectroscopic Identification of Organic Compounds*, Wiley, New York, 1991, p. 289–315.
17 V. Gaidelis, L. Jelenskis, E. Montrimas and D. Jurevicius, *Lithuanian J. Phys.*, 1984, **24**, 80–89.
18 Ch. Beginn, J. V. Grazulevicius, P. Strohriegl, J. Simmerer and D. Haarer, *Macromol. Chem. Phys.*, 1994, **195**, 2353–2370.
19 S. Grigalevicius, G. Blazys, J. Ostrauskaite, J. V. Grazulevicius, V. Gaidelis, V. Jankauskas and E. Montrimas, *Synth. Met.*, 2002, **128**, 127–131.
20 M. Daskeviciene, V. Gaidelis, V. Getautis, V. Jankauskas, O. Paliulis and J. Sidaravicius, *Lithuanian J. Phys.*, 2001, **41**, 521–526.
21 P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems*, Marcel Dekker, New York, 1993, p. 273.
22 J. Kalade, E. Montrimas and V. Jankauskas, in *Proc. ICPS'94: The Physics and Chemistry of Imaging Systems*, Rochester, 1994, p. 747.
23 R. M. Schaffert, *Electrophotography*, The Focal Press, London and New York, 1965, p. 203.