

3,3'-Bicarbazole-based dihydrazones for electrophotographic photoreceptors

Asta Michalevičiūtė¹,
Gintaras Buika¹,
Jolita Ostrauskaitė¹,
Juozas Vidas Gražulevičius¹,
Vygintas Jankauskas²,
François Tran-Van³ and
Claude Chevrot³

¹ Department of Organic Technology,
Kaunas University of Technology,
Radvilėnø pl. 19, LT-50254 Kaunas,
Lithuania

² Department of Solid State Electronics,
Vilnius University, Sauletekio aleja 9,
LT 10222, Vilnius, Lithuania

³ Laboratoire de Physico-Chimie des
Polymères et des Interfaces,
Université de Cergy-Pontoise,
5 mail Gay-Lussac, 95031,
Cergy-Pontoise Cedex, France

Two 3,3'-bicarbazole-based dihydrazones have been synthesized. The optical, thermal and photoelectrical properties of these compounds have been investigated. The new dihydrazones absorb electromagnetic radiation of 200–420 nm and form glasses with the glass transition temperatures 70–72 °C. The ionization potentials of newly synthesized dihydrazones are 5.31–5.33 eV. The hole-drift mobility of amorphous films of the solid 50 wt.% solutions of 3,3'-bicarbazole-based dihydrazones in bisphenol Z polycarbonate approach 10^{-4} cm²/(Vs) at high electric fields.

Key words: carbazole, hydrazone, molecular glass

INTRODUCTION

Carbazole-containing and other aromatic hydrazones exhibit relatively high hole-drift mobilities [1]. The electrographic photoreceptors with these molecules, dispersed in polymer hosts, show excellent performance [2, 3]. The main advantage of low-molar-mass charge-transporting glasses against crystalline materials is their ability to form amorphous transparent films on substrates. In electrographic photoreceptors the mechanical properties of which are of great importance, the charge transport layer is prepared by imbedding an organic charge transporting material into a polymer matrix, *e.g.*, polycarbonate. A charge transport layer has to contain a large amount (up to

50% or even more) 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 that do not readily crystallize are needed.

Herewith we report on the synthesis and properties of new glass-forming 3,3'-bicarbazole-based dihydrazones for electrographic photoreceptors.

EXPERIMENTAL

Instrumentation

¹H NMR and ¹³C NMR spectra were obtained on a Avanse 250 (250 MHz) instrument. IR-spectroscopy was performed on Perkin-Elmer Spectrum GX spectrophotometers, using KBr pellets. UV-VIS spectra

* Corresponding author, E-mail: juozas.grazulevicius@ktu.lt

were recorded with a Hitachi U3000 spectrophotometer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 20 instrument at 10 K/min heating rate under N₂ atmosphere. The ionisation potential (I_p) was measured by the electron photoemission in air method as described before [2]. Hole drift mobility was measured by the xerographic time-of-flight method [4].

Materials

3,3'-bi(9-hexylcarbazole) (1). The solution of 4 g (15.9 mmol) of 9-hexylcarbazole in 10 ml of chloroform was added to the solution of 7.74 g (47.7 mmol) of FeCl₃ in 40 ml of CHCl₃. This mixture was stirred for 18 h. at room temperature, then filtered and washed with chloroform. The precipitates were stirred in water / ammonia mixture (60 ml / 30 ml (28%)) for 0.5 h and then extracted with 1,2-dichloromethane. The extract was dried with Na₂SO₄, and the solvent was evaporated. Yield, 3 g (75%).

¹H NMR (250 MHz, DMSO-d₆, δ, m.d.): 0.83–0.89 (t, 6H, CH₃), 1.25–1.45 (m, 12H, CH₂), 1.87–1.98 (m, 4H, CH₂), 4.30 (t, 4H, -CH₂-N), 7.42–7.49 (m, 8H, Ar), 7.79 (d, 2H, Ar), 8.15 (d, 2H, Ar), 8.39 (d, 2H, Ar). IR (KBr, cm⁻¹): 3050 (Ar C-H), 2953, 2930, 2875 (Alk C-H), 1599, 1490 (Ar C=C). MS: m/z = 501 (M⁺).

3,3'-bi(9-hexylcarbazol-6-carbaldehyde) (2). The solution of 1.5 g (3 mmol) of 3,3'-bi(9-hexylcarbazole) (1) in 2 ml of fresh distilled o-dichlorobenzene was added dropwise to a mixture of 0.84 ml POCl₃ (9 mmol) and 0.74 ml (9.6 mmol) DMF at 0 °C under argon atmosphere. This mixture was let to warm up to room temperature slowly and then stirred at 90–100 °C for 4 h. The reaction mixture was cooled to 25 °C and extracted with 1,2-dichloromethane. The product was purified by silica gel column chromatography with an eluent mixture of chloroform and hexane in a volume ratio of 3:2. Yield, 1.53 g (92%).

¹H NMR (250 MHz, CDCl₃, δ, m.d.): 0.88–0.89 (t, 6H, CH₃), 1.29–1.47 (m, 12H, CH₂), 1.87–1.96 (m, 4H, CH₂), 4.31–4.37 (t, 4H, -CH₂-N), 7.47 (d, 2H, Ar), 7.56 (d, 2H, Ar), 7.92 (d, 2H, Ar), 8.00 (d, 2H, Ar), 8.46 (s, 2H, Ar), 8.68 (s, 2H, Ar), 10.10 (s, 2H, -CHO). IR (KBr, cm⁻¹): 3050 (Ar C-H), 2953, 2930, 2917, 2875 (alk C-H), 1690 (C=O), 1599, 1490 (Ar C=C). MS: m/z = 557 (M⁺).

3,3'-bi(9-hexylcarbazol-6-carbaldehyde N-methyl-N-phenylhydrazone) (3a). A mixture of 0.7 g (1.26 mmol) 3,3'-bi(9-hexylcarbazol-6-carbaldehyde) (2) and 1-methyl-1-phenylhydrazine (5 mmol) in ethanol was refluxed for 5 h. The formed precipitates were filtered off. The product was purified by silica gel column chromatography with an eluent mixture of hexane and dichloromethane in a volume ratio of 1:1. Yield, 0.59 g (61%).

¹H NMR (250 MHz, CDCl₃, δ, m.d.): 0.87–0.92 (t, 6H, CH₃), 1.29–1.41 (m, 12H, CH₂), 1.86–1.99 (m, 4H, CH₂), 3.47 (s, 6H, N-CH₃), 4.31–4.36 (t, 4H, -CH₂-N), 7.30–7.51 (m, 14H, Ar), 7.76 (s, 2H, NH), 7.81–7.85 (m, 2H, Ar), 7.93–7.96 (d, 2H, Ar), 8.43–8.45 (m, 4H, Ar). ¹³C NMR (250 MHz, CDCl₃, δ, m.d.): 14.45 (CH₃), 22.98 (CH₂), 27.41 (CH₂), 29.47 (CH₂), 30.11 (CH₂), 33.59 (N-CH₃), 43.77 (N-CH₂), 109.44, 115.51, 119.13, 119.54, 120.45, 123.67, 123.97, 124.5, 126.0, 128.5, 129.4, 134.0, 140.3, 141.3 (Ar), 148.6 (CH=N). IR (KBr, cm⁻¹): 3050 (Ar C-H), 2952, 2942, 2917, 2946 (Alk C-H), 1630 (C=N), 1596, 1498 (Ar C=C), 1249 (C-N). Elemental analysis. Found, %: C 81.72; N 10.13; H 7.72. C₅₂H₅₆N₆. Calculated, %: C 81.64; N 10.98; H 7.38. MS: m/z = 765 (M⁺).

3,3'-bi(9-hexylcarbazol-6-carbaldehyde N,N-diphenylhydrazone) (3b) was synthesized from 0.8 g (1.44 mmol) 3,3'-bi(9-hexylcarbazol-6-carbaldehyde) (2) and 1,1-diphenylhydrazine hydrochloride (5.7 mmol) by the same procedure as **3a**. Yield, 0.7 g (50%).

¹H NMR (250 MHz, CDCl₃, δ, m.d.): 0.83–0.89 (t, 6H, CH₃), 1.28–1.37 (m, 12H, CH₂), 1.90 (m, 4H, CH₂), 4.32 (t, 4H, -CH₂-N), 7.16–7.21 (m, 5H, Ar), 7.27 (m, 5H, Ar), 7.37–7.48 (m, 16H, Ar), 7.77–7.81 (m, 2H, Ar), 7.89–7.93 (m, 2H, Ar), 8.25–8.26 (d, 2H, Ar), 8.36–8.37 (d, 2H, Ar). ¹³C NMR (250 MHz, CDCl₃, δ, m.d.): 14.44 (CH₃), 22.96 (CH₂), 27.39 (CH₂), 29.45 (CH₂), 32.00 (CH₂), 43.75 (N-CH₂), 109.44, 119.43, 119.66, 123.00, 123.93, 124.45, 124.56, 125.97, 127.76, 130.11, 133.9, 137.87, 140.27, 141.52 (Ar), 144.5 (CH=N). IR (KBr, cm⁻¹): 3050 (Ar C-H), 2949, 2922, 2865, 2850 (Alk C-H), 1630 (C=N), 1588, 1492 (Ar C=C), 1239 (C-N). Elemental analysis. Found, %: C 83.74; N 9.12; H 6.69. C₆₂H₆₀N₆. Calculated, %: C 83.75; N 9.45; H 6.80. MS: m/z = 889 (M⁺).

RESULTS AND DISCUSSION

Two 3,3'-bicarbazole-based dihydrazones were synthesized by a three-step synthetic route shown in Fig. 1. The first step was the oxidative dimerization of 9-hexylcarbazole with FeCl₃ to get 3,3'-bi(9-hexylcarbazole) (1). The second step was the synthesis of dialdehyde 2, and the last step was the condensation of 3,3'-bi(9-hexylcarbazol-6-carbaldehyde) 2 with hydrazines having different substituents to get the final compounds: 3,3'-bi(9-hexylcarbazol-6-carbaldehyde N-methyl-N-phenylhydrazone) **3a** and 3,3'-bi(9-hexylcarbazol-6-carbaldehyde N,N-diphenylhydrazone) **3b**.

The structure of the synthesized compounds was confirmed by ¹H NMR, ¹³C NMR, IR spectroscopy and elemental analysis (see Experimental section).

The morphological properties of compounds **3a** and **3b** were studied by differential scanning calorimetry (DSC). DSC measurements have shown that

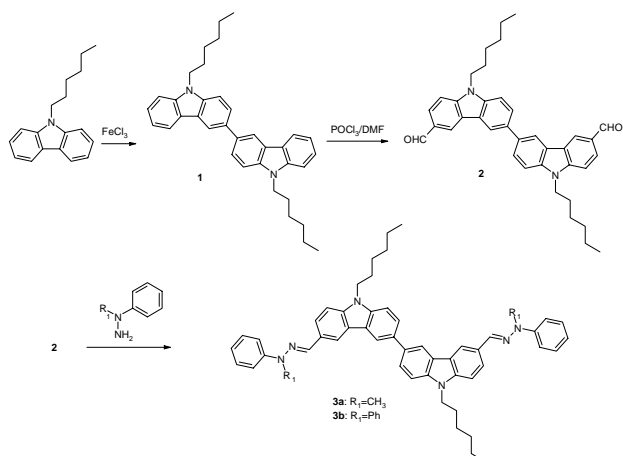


Fig. 1. Synthesis of 3,3'-dicarbazyl-based dihydrazones

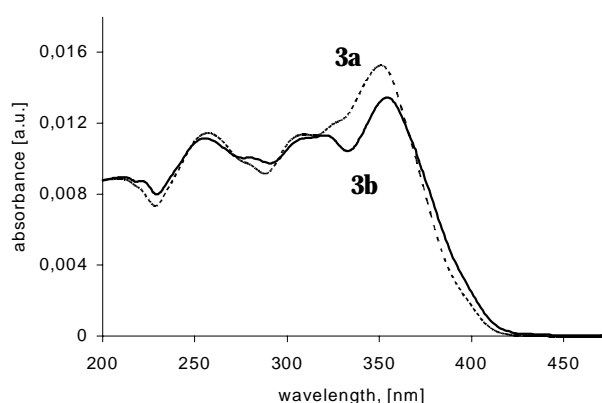


Fig. 2. UV/VIS absorption spectra of dilute solutions of 3,3'-dicarbazyl-based dihydrazones **3a** and **3b** in chloroform (10^{-5} mol/l)

both compounds form glasses after cooling of the melted samples ($T_m = 220$ °C for **3a**, $T_m = 240$ °C for **3b**). The glass transition temperatures (T_g) are: 70 °C for **3a** and 72 °C for **3b**. The T_g values of the compounds are very close. This observation shows that the substitution of methyl substituents by bigger phenyl substituents in the molecules does not create a steric interference for molecular motion. Amorphous films of the synthesized dihydrazones on substrates can be prepared by spin-coating or casting techniques.

The optical properties of compounds **3a** and **3b** were investigated by UV-VIS spectroscopy. Both dihydrazones absorb electromagnetic radiation in the range of 200–420 nm (Fig. 2). The substitution of methyl group by phenyl group in the nitrogen atom of the hydrazone moiety leads to a small bathochromic shift of 4 nm of the lowest energy absorption band (cf. UV spectra of **3a** and **3b**).

The ionization potentials (I_p) of the films 3,3'-bicarbazole-based dihydrazones **3a** and **3b** were established from their electron photoemission spectra (Fig. 3.). The I_p value of 5.31 eV was established for compound **3a** and that of 5.33 eV was observed for compound **3b**. These I_p values show that compounds

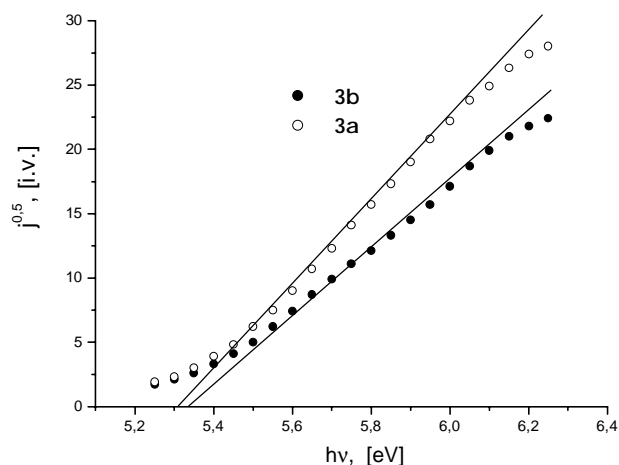


Fig. 3. Electron photoemission spectra of amorphous films of 3,3'-dicarbazyl-based dihydrazones

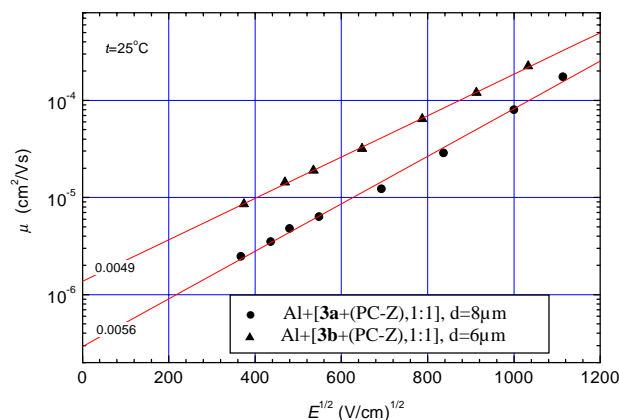


Fig. 4. Electric field dependencies of hole-drift mobilities (μ) in amorphous films of 3,3'-dicarbazyl-based dihydrazones **3a** and **3b** doped in PC-Z (50 wt.%)

3a and **3b** are suitable for the application in electrographic photoreceptors. Holes are easily injected into the charge transport layer from a charge generation layer with I_p close to I_p of the charge transport layer. The I_p values for charge generation materials widely used in electrographic photoreceptors such as titanil phthalocyanines, perylene pigments and bisazo pigments are in the range of 5.1–5.6 eV [5].

The time-of-flight technique was used to characterize hole-drift mobility in amorphous films of compounds **3a** and **3b** molecularly doped in polymeric host bisphenol Z polycarbonate (PC-Z) (50 wt.% of **3a** and **3b**). The room temperature hole mobilities (μ) of these materials show linear dependencies on the square root of the electric field (Fig. 4). This observation is characteristic of the majority of non-crystalline organic semiconductors and is attributed to the effects of disorder on charge transport [5]. The hole-drift mobility values in both materials are similar, and at high electric fields they exceed 10^{-4} $\text{cm}^2/(\text{Vs})$. These are relatively high values for mole-

cularly doped polymers. For the amorphous films of pure compounds **3a** and **3b**, hole mobility approaching 10^{-2} cm²/(Vs) can be predicted.

CONCLUSIONS

Glass-forming 3,3'-bicarbazole-based dihydrazones have been synthesized and their optical, thermal and photoelectrical properties have been studied. These dihydrazones absorb light in the range of 200–420 nm. They form glasses with the glass transition temperatures of 70 and 72 °C. The ionization potentials of new dihydrazones are 5.31 and 5.33 eV. Hole-drift mobility in the amorphous films of the 50 wt.% solid solutions of 3,3'-bicarbazole-based dihydrazones in bisphenol Z polycarbonate exceed 10^{-4} cm²/(Vs) at high electric fields. The results obtained show that the synthesized compounds are suitable for the application in electrographic photoreceptors.

ACKNOWLEDGEMENTS

This work was performed in the frame of the Gilbert programme of scientific and technological collaboration between France and Lithuania. Habil. Dr. V. Gaidelis from the Department of Solid State Electronics, Vilnius University is thanked for the ionization potential measurements.

Received 09 September 2005

Accepted 26 September 2005

References

1. P. Stroehriegl and Grazulevicius J. V., *Adv. Mater.*, **14**(20), 1439 (2002).
2. J. Ostrauskaite, V. Voska, J. Antulis, V. Gaidelis, V. Jankauskas and J. V. Grazulevicius, *J. Mater. Chem.*, **12**(12), 3469 (2002).
3. J. Ostrauskaite, V. Voska, G. Buika, V. Gaidelis, V. Jankauskas, H. Janeczek, J. D. Sidaravicius and J. V. Grazulevicius, *Synth. Met.*, **138**, 457 (2003).
4. J. Kalade, E. Montrimas, V. Jankauskas, in *Proc. ICPS'94: The Physics and Chemistry of Imaging Systems*, p. 747, Rochester (1994).
5. M. Borsenberger and D. S. Weiss, *Photoreceptors for imaging systems*, 273 p., New York: Marcel Dekker (1993).

Asta Michalevičiūtė, Gintaras Buika, Jolita Ostrauskaitė,
Juozas Vidas Gražulevičius, Vygintas Jankauskas,
Francois Tran-Van, Claude Chevrot

ELEKTROGRAFINIAMS FOTORECEPTORIAMS SKIRTI 3,3'-BIKARBAZOLILDIHIDRAZONAI

Santrauka

Susintetinti du nauji 3,3-bi(karbazolildihidrazonai) bei ištirtos jų optinės, morfologinės ir fotoelektrinės savybės. Šie dihidrazonai absorbuoja elektromagnetinę spinduliuotę 200–420 nm bangų ilgio diapazone. Diferencinės skenuojamosios kalorimetrijos metodu nustatyta, kad naujieji 3,3'-bi(karbazolildihidrazonai) sudaro stiklus, kurių stiklėjimo temperatūros yra 70 ir 72°C. Elektronų fotoemisijos ore metodu nustatyti šių dihidrazonų jonizacijos potencialai yra 5,31 ir 5,33 eV. Lėkio trukmės metodu nustatyta, kad skylių dreifiniai judriai 3,3'-bikarbazolo dihidrazonų 50 masės % kiektuosiuose tirpaluose bisfenolio Z polikarbonate stipriuose elektriniuose laukuose siekia 10^{-4} cm²/(V·s). Gauti rezultatai rodo, kad susintetinti 3,3'-bi(karbazolildihidrazonai) gali būti panaudoti elektrografiniuose fotoreceptoriuose.