# High Hole Mobilities in the Amorphous Films of 2,7-Di(9-carbazolyl)-9-(2-ethylhexyl)carbazole

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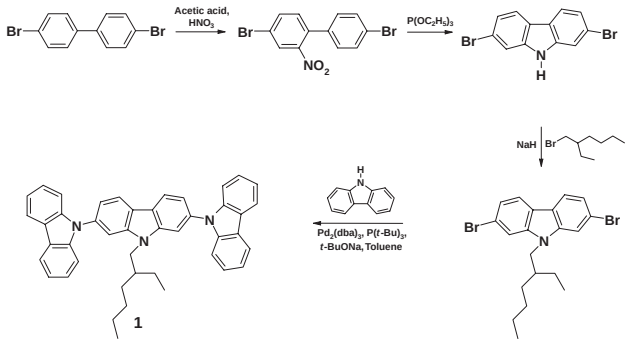
2,7-Di(9-carbazolyl)-9-(2-ethylhexyl)carbazole was synthesized and investigated as new effective hole-transporting material. The synthesized compound showed high thermal stability with the initial weight loss temperature of 400 °C. It forms glass with glass-transition temperature of 88 °C. Hole drift mobilities in the amorphous films of the newly synthesized compound exceeded $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ at high electric field, as characterized by the xerographic time of flight technique.

Amorphous film-forming hole-transporting materials are known for various electronic and optoelectronic applications.[1–3] Glass-forming semiconductors with high charge mobilities are of particular interest for the application in organic-thin-film transistors and solar cells. Compounds containing 2,7-substituted carbazole unit represent a class of effective hole-transporting materials.[4] The aim of this work was synthesis of new 2,7-dicarbazolyl-substituted carbazole derivative and estimation of its charge-transport properties. There is a substantial number of studies on 3,6-disubstituted carbazole compounds, including small molecules, oligomers, and polymers for optoelectronic applications. However, there are only few studies on low-molecular-weight 2,7-disubstituted carbazole compounds so far. The main obstacle was the lack of an efficient synthesis procedure for these compounds. Leclerc and co-workers[5] and Mullen and co-workers[6] reported convenient synthetic pathways towards 2,7-dihalocarbazoles, which are useful precursors for carbazole-based optoelectronic materials.

2,7-Di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (**1**) was obtained as described in Scheme 1 by the synthetic route, comprising N-alkylation of 2,7-dibromo-9*H*-carbazole with 2-ethylhexyl bromide to form 2,7-dibromo-9-(2-ethylhexyl)-carbazole and a palladium-catalyzed aromatic C–N coupling reaction of the later with carbazole. The synthesized compound **1** was purified by column chromatography followed by crystallization from hexane to obtain pure and well-defined compound. Compound **1** was characterized by $^1$H NMR, IR, mass spectrometries, and elemental analysis.[7]




**Scheme 1.** Outline of the synthetic route.

The glass-forming capability and thermal stability of 2,7-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (**1**) were estimated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Compound **1** exhibited melting isotherm during the first DSC heating scan, but cooling of the melt led to the formation of a glassy state that persisted in the subsequent DSC scans (Figure 1). Compound **1** appeared to have considerably lower glass-transition temperature ($T_g$) than the earlier synthesized 3,6-disubstituted carbazole derivative of very similar structure, i.e. 3,6-di(9-cabazolyl)-9-octylcarbazole.[8] $T_g$ of **1** was found to be 88 °C while the 3,6-di(9-carbazolyl)-9-octylcarbazole showed $T_g$ of 134 °C. The 1% weight loss temperature ($T_d$) for the 2,7-disubstituted carbazole compound **1** (400 °C) was found to be higher than that for 3,6-di(9-cabazolyl)-9-octylcarbazole (375 °C).

UV absorption spectra of the dilute solution of compound **1** is given in Figure 2. For the comparison the spectrum of 3,6-di(9-cabazolyl)-9-octylcarbazole is also shown. The lowest energy absorption band of compound **1** is hyperchromically and bathochromically shifted with respect to that of 3,6-di(9-cabazolyl)-9-octylcarbazole.

The ionization potential ($I_p$) was measured by electron photoemission in air.[9] The $I_p$ value for the film of compound **1** was found to be 5.83 eV. 3,6-Di(9-carbazolyl)-9-octylcarbazole showed very similar $I_p$ value of 5.80 eV. Using the value of optical band gap ($\Delta E$) which can be estimated by the absorption spectroscopy, a LUMO value of 2.45 eV was calculated for **1** by the method described before.[10]

Hole-transport properties of compound **1** were studied by the xerographic time-of-flight method. Representative $dU/dt$ transient for the amorphous films of 2,7-disubstituted carbazole compound **1** is shown in Figure 3. It shows dispersive hole transport. The dispersive charge transport was also observed for 3,6-di(9-cabazolyl)-9-octylcarbazole.[8]

The hole-transit times ($t_T$) needed for the estimation of hole mobilities were established from intersection points of two

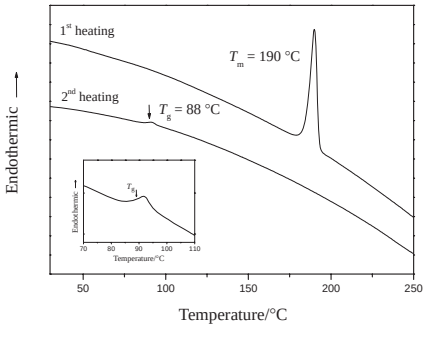



**Figure 1.** DSC curves of compound **1**, at the heating/cooling rate of 10 °C min$^{-1}$, $N_2$ atmosphere.

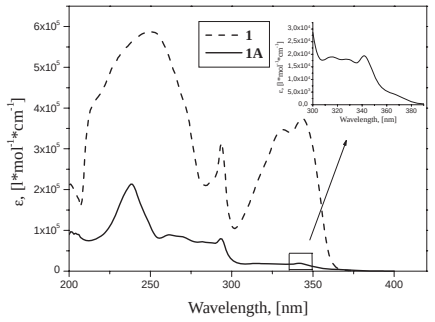



**Figure 2.** UV absorption spectra of the dilute THF solutions ($10^{-5}$ M) of compound **1** and 3,6-dicabazolyl-9-octylcarbazole.

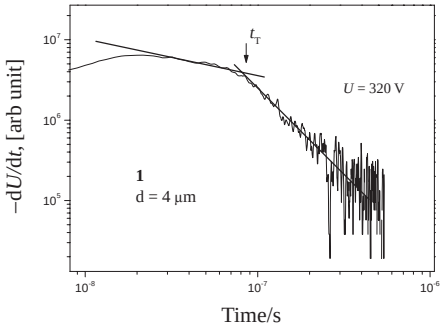



**Figure 3.** Time-of-flight transient for amorphous 4 μm thick layer of **1** ($U$ is the surface voltage).

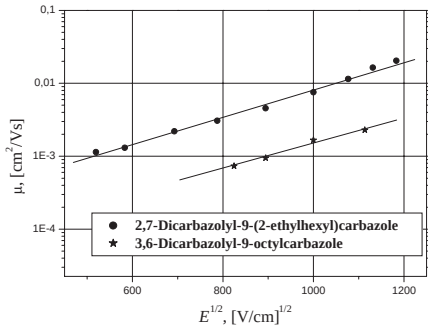



**Figure 4.** The electric field dependencies of the hole drift mobilities in the amorphous films of compound **1** and 3,6-di(9-cabazolyl)-9-octylcarbazole.

asymptotes from the double-logarithmic plots. The obtained hole mobilities are shown in Figure 4 as a function of the square root of electric field ($E^{1/2}$). For the comparison electric field dependence of hole mobility is shown also for the amorphous film of 3,6-di(9-cabazolyl)-9-octylcarbazole.

The field dependence of the hole mobilities ($\mu$) follows the nearly universal Poole–Frenkel relationship: $\mu = \mu_0 \exp(\alpha\sqrt{E})$, which is usually observed for disordered organic systems, where $\alpha$ is the Poole–Frenkel factor.[11] Hole mobilities in the amorphous film of compound **1** well exceed $10^{-2}$ $cm^2\ V^{-1}\ s^{-1}$ at high electric fields. They are by almost one order of magnitude higher than those observed for 3,6-di(9-cabazolyl)-9-octylcarbazole. The more extended conjugation network in 2,7-disubstituted carbazole may result in stronger electronic coupling between molecules, thereby facilitating hole hopping. It is also possible that different linking topologies (and thus conformations) in 2,7- and 3,6-disubstituted carbazoles lead to significant differences in molecular packing, which in turn affect the molecular packing density and the positional disorder in thin films, which are critical for hole transport.

Financial support of this research by the Lithuanian Science and Studies Foundation is gratefully acknowledged.

## References and Notes

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7 Compound **1**: mp. 188–189 °C. A $^1$H NMR spectrum yielded the following chemical shifts (300 MHz, $CDCl_3$), $\delta$ 0.83 (t, $J = 6.45$ Hz, 3H, $CH_3$), 0.95 (t, $J = 7.30$ Hz, 3H, $CH_3$), 1.25–1.51 (m, 8H, $CH_2$), 2.11–2.19 (m, 1H, CH), 4.23 (d, $J = 7.34$ Hz, 2H, $NCH_2$), 7.37 (d, $J = 1.10$ Hz, 1H), 7.39 (d, $J = 1.46$ Hz, 2H), 7.42 (d, $J = 1.10$ Hz, 1H), 7.48–7.60 (m, 10H), 7.69 (d, $J = 1.84$ Hz, 2H), 8.27 (d, $J = 7.33$ Hz, 4H), 8.40 (d, $J = 8.02$ Hz, 2H). IR (KBr), $\nu$ ($cm^{-1}$); (arene C–H) 3042, 3021; (aliphatic C–H) 2952, 2925, 2853; (C=C in Ar) 1496, 1459. MS (APCl$^+$, 20 V), $m/z$ (%) 610 ([M + H]$^+$, 100). Anal. Calc. for $C_{44}H_{39}N_3$: C, 86.66; H, 6.45; N 6.89%. Found: C, 86.70; H 6.50; N 6.92%.
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Published on the web (Advance View) February 23, 2008; doi:10.1246/cl.2008.344