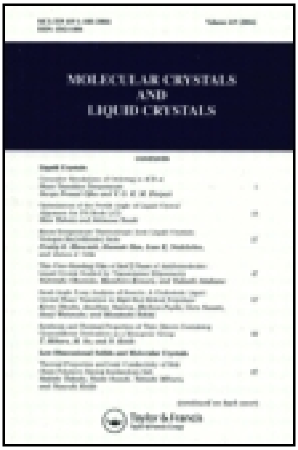

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New Carbazolyl Containing Molecular Glasses for Optoelectronics

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The multistep synthesis, characterization and properties of the well defined six carbazolyl and branched aliphatic chain containing organic photosemiconductor is reported. It was prepared by the nucleophilic opening of the oxirane cycle of 1,6-di(carbazol-9-yl)-5-(carbazol-9-methyl)-4-oxa-2-hexanol glycidyl ether with the linking agent 4,4′-thiobisbenzenethiol in the presence of catalyst triethylamine (TEA). The molecular structure of this branched molecular glass prevents its crystallization in the layer and allows stable films to be prepared without binder material. The hole drift mobility, measured by the time-of-flight technique, reaches $10^{-5}\,cm^2/V\cdot s$ *at an electric field of* $10^6\,V\cdot cm^{-1}$. *The value of ionization potential (5.92 eV) measured by the electron photoemission method in air is close to those reported for the other organic photoconductors containing electronically isolated carbazolyl moieties.*

Keywords: 1-chloro-2,3-epoxypropane; 4,4′-thiobisbenzenethiol; carbazole; charge transport; hole drift mobility; ionization potential; molecular glass

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INTRODUCTION

Since discovery of photoconductivity in poly-(9-vinylcarbazole) (PVC) and others polyvinyl derivatives having a pendant carbazole group, also polymers and oligomers of 9-(2,3-epoxypropyl)carbazole (PEPC) are among the most widely studied photoconductive materials for applications in electrophotography, light emitting diodes, photorefractive materials [1–3]. In 1980's the synthesis of well defined low-molecular-mass photoconductive compounds which are able to form amorphous films on substrates, including flexible ones, was developed [4,5]. Low-molecular-mass compounds that are capable of existing in amorphous state have been called molecular glasses or amorphous molecular materials [6]. Such compounds were prepared by the reaction of epoxypropyl group containing photoconductive materials with different bifunctional compounds, such as aromatic diols, dimercapto compounds and derivatives of aniline [7,8]. They possess four photoconductive groups, linked by the branched aliphatic chain and π-conjugation between those groups is isolated. High morphological stability of such molecular glasses is explained by the existance of several diastereoisomers, possibility of intermolecular hydrogen bonding and flexibility of the aliphatic linking chains [8]. Despite the lower concentration of the chromophores, hole drift mobilities measured in such molecular glasses reach $10^{-4}\,\mathrm{cm^2/V\cdot s}$ at an electric field of $10^6\,\mathrm{V\cdot cm^{-1}}$ and thus exceeds the parameters of the well known carbazolyl containing polymers (PVC, PEPC). The aim of our work was synthesis and investigation of the properties of analogous hole-transporting compounds with increased number of carbazolyl chromophores using 1,6-di(carbazol-9-yl)-5-(carbazol-9-methyl)-4-oxa-2-hexanol glycidyl ether instead of 1,3-di(carbazol-9-yl)-2-propanol glycidyl ether.

EXPERIMENTAL

Materials

1-Chloro-2,3-epoxypropane, 4,4′-thiobisbenzenethiol were purshased from "Aldrich".

1,3-Di(carbazol-9-yl)-2-propanol (1). 16.7 g (0.1 mol) of carbazole and 22.3 g (0.1 mol) of 9-(2,3-epoxypropyl)carbazole were dissolved in 50 mL butanone. After the cooling the solution to the room temperature 9.9 g (0.15 mol) of 85% powdered KOH and 7.1 g (0.05 mol) of anhydrous Na_2SO_4 were added and the mixture was stirred at 30–35°C. After completion of the reaction (Silufol UV-254, eluent – acetone-hexane, 7:5), the mixture was poured into water (200 mL).

The formed precipitate was filtered off, washed with distilled water until the wash water was neutral and dried. The yield was 32.9 g (84.5%) (mp 153.5–154°C (toluene)). IR (KBr), $\bar{\nu}$, cm^{-1}: 3536 (OH); 3049 (CH_{arom}); 2968, 2939, 2891 (CH_{aliph}); 1626, 1596, 1484, 1453 (C=C, C−N); 751, 722 (C=C of Ht). ^1H NMR (300 MHz, $CDCl_3$), δ, ppm: 8.06–8.00 (m, 4H, 4-H, 5-H Ht); 7.42–7.09 (m, 12H, Ht); 4.64–4.50 (m, 1H, $NCH_2C\underline{H}$); 4.34 (dd, AB part of ABX system, $J_{AB} = 14.8$ Hz, $J_{AX} = 7.6$ Hz, 2H, *trans*-H_A of $2 \times NC\underline{H}_2$); 4.22 (dd, $J_{BX} = 4.9$ Hz 2H, *cis*-H_B of $2 \times NC\underline{H}_2$); 1.91 (s, 1H, $CH(\underline{OH})$).

1,3-Di(carbazol-9-yl)-2-propanol glycidyl ether (2). To the solution of compound **1** (39.0 g, 0.1 mol) in 100 mL butanone 92.5 g (1 mol) of 1-chlor-2,3-epoxypropane (CEP), 19.6 g (0.3 mol) of 85% powdered KOH and 14.2 g (0.1 mol) of anhydrous Na_2SO_4 were added. The mixture was stirred at 25–30°C temperature until **1** was completely consumed. After termination of the reaction (Silufol UV-254, eluent – diethyl ether-hexane, 1:1), the mixture was treated with toluene and water. The organic layer was washed with distilled water until the wash water was neutral, dried over anhydrous Mg_2SO_4, treated with activated charcoal and filtered off. Toluene was removed and the residue was dissolved in toluene. The crystals formed upon standing were filtered off and washed with 2-propanol. The yield was 37.3 g (83.7%) (mp 92.5–94°C (toluene)). IR (KBr), $\bar{\nu}$, cm^{-1}: 3047, 2998 (CH_{arom}); 2964, 2936, 2886 (CH_{aliph}); 1626, 1597, 1576, 1484, 1460, 1453 (C=C, C−N); 1254, 849 (cycle of oxirane); 1124, 1100 (C−O−C); 750, 721 (C=C of Ht). ^1H NMR (300 MHz, $CDCl_3$), δ, ppm: 8.06 (2d, $J = 8.2$ Hz, Hz, 4H, 4-H, 5-H Ht); 7.46–7.13 (m, 12H, Ht); 4.60–4.13 (m, 5H, NCH_2CHCH_2N); 3.02 (dd, AB part of ABX system, $J_{AB} = 11.7$ Hz, $J_{AX} = 3.7$ Hz, 1H, *trans*-H_A of $OC\underline{H}_2$); 2.94 (dd, $J_{BX} = 5.5$ Hz 1H, *cis*-H_B of $OC\underline{H}_2$); 2.51–2.43 (m, 1H, OCH of oxirane cycle), 2.31 (dd, AB part of ABX system, $J_{AB} = 9.3$ Hz, $J_{AX} = 4.5$ Hz, 1H, *cis*-H_A of OCH_2 of oxirane cycle); 2.01 (dd, $J_{BX} = 1.6$ Hz 1H, *trans*-H_B of OCH_2 of oxirane cycle).

1,6-Di(carbazol-9-yl)-5-(carbazol-9-methyl)-4-oxa-2-hexanol (3). 44.65 g (0.1 mol) of **2** and 16.7 g (0.1 mol) of carbazole were dissolved in 400 mL butanone. After the cooling the solution to the room temperature 13.2 g (0.2 mol) of 85% powdered KOH and 7.1 g (0.05 mol) of anhydrous Na_2SO_4 were added and the mixture was stirred at 35°C for 24 h. After termination of the reaction (Silufol UV-254, eluent – diethyl ether-hexane, 1:1), the product was isolated analogously as compound **2**. The yield was 43 g (70.1%) (mp 118–120°C). IR (KBr), $\bar{\nu}$, cm^{-1}: 3521 (OH); 3052, 3022 (CH_{arom}), 2962, 2931, 2880 (CH_{aliph}); 1626, 1597, 1485, 1461, 1453 (C=C, C−N); 750, 722 (C=C of Ht). ^1H NMR (300 MHz, $CDCl_3$), δ, ppm: 8.10–7.97 (m, 6H, 4-H, 5-H Ht); 7.60–6.90 (m, 18H, Ht); 4.51–4.11 (m, 5H, NCH_2CHCH_2N); 3.80 (dd, AB part of ABX system, $J_{AB} = 16.6\,Hz$, $J_{AX} = 6.2\,Hz$, 1H, *trans*-H_A of $NC\underline{H}_2CHCH_2O$); 3.71 (dd, $J_{BX} = 6.6\,Hz$ 1H, *cis*-H_B of $NC\underline{H}_2CHCH_2O$); 3.65–3.56 (m, 1H, $C\underline{H}OH$) ; 2.99–2.89 (m, 2H, $CHOC\underline{H}_2$), 1.43 (s, 1H, $CH(O\underline{H})$.

1,6-Di(carbazol-9-yl)-5-(carbazol-9-methyl)-4-oxa-2-hexanol glycidyl ether (4). 50 g (0.0815 mol) of **3**, 113.16 g (1.223 mol, 95.7 mL) of CEP, 16.18 g (0.245 mol) of 85% powdered KOH and 5.82 g (0.041 mol) of anhydrous Na_2SO_4 were stirred at 35°C for 24 hours. After termination of the reaction (Silufol UV-254, eluent – diethyl ether-hexane, 1:1), the product was isolated analogously as compound **2**. The yield was 31.7 g (58.2%) (mp 108.5–109°C). IR (KBr), $\bar{\nu}$, cm^{-1}: 3049 (CH_{arom}); 2937, 2873 (CH_{aliph}); 1626, 1596, 1485, 1454 (C=C, C–N); 1253, 852 (cycle of oxirane); 1109, 1094 (C–O–C); 752, 723 (C=C of Ht). ^1H NMR (300 MHz, $CDCl_3$), δ, ppm: 8.19–7.96 (m, 6H, 4-H, 5-H Ht); 7.55–7.04 (m, 18H, Ht); 4.64–4.18 (m, 5H, NCH_2CHCH_2N); 3.90–3.68 (m, 2H, $NC\underline{H}_2CHCH_2O$); 3.37–3.18 (m, 1H, $NCH_2C\underline{H}$ CH_2O), 3.06–2.87 (m, 2H, $OC\underline{H}_2CHCH_2N$); 2.83–1.44 (m, 5H, CH_2CHCH_2 of 2,3-epoxypropyl group).

4,4′-Bis[10-(carbazol-9-yl)-6,9-(carbazol-9-methyl)-3-hydroxy-5,8-dioxa-1-tia]tiobisbenzene (5). 3 g (0.0045 mol) of **4** was dissolved in 15 ml of DMF by heating and 0.53 g (0.0021 mol) of 4,4′-thiobis-benzenethiol, 0.25 mL (0.0018 mol) of TEA were added. The reaction mixture was refluxed under argon for 1 h. After completion of the reaction (Silufol UV-254, eluent – acetone-hexane, 7:18), DMF and TEA were removed and the product was purified by column chromatography using acetone-hexane (1:4) as the eluent. Fraction containing resulting product was collected and the eluent was evaporated. Then the 20% solution of the resulting product in toluene (21 mL) was prepared and poured with intensive stirring into a 20-fold excess of hexane. The product was filtered off and washed with hexane to yield 2.45 g (62.2%) of amorphous **5**. IR (KBr), $\bar{\nu}$, cm^{-1}: 3600–3300 (OH); 3049, 3022 (CH_{arom}); 2927, 2870 (CH_{aliph}); 1626, 1597, 1485, 1453 (C=C, C–N); 812 (C=C of 1,4-di-substituted benzene); 750, 721 (C=C of Ht).

MEASUREMENT

The ^1H NMR spectra were recorded in deuterochloroform ($CDCl_3$) using a Varian Unity Inova (300 MHz) spectrometer, the chemical shifts are expressed in ppm, downfield from tetramethylsilane (TMS), used as internal standard. The symbols d, m, t, s were respectively used for doublet, multiplet, triplet and singlet. The IR spectra were taken for samples in KBr pellets on a Perkin Elmar Spectrum GX FT-IR system spectrometer. The UV spectra were recorded on a Spectronic Genesys 8 spectrometer and the fluorescence spectra – on a Hitachi MPF-4 spectrophotometer. 10^{-4} M solutions in THF of investigated materials and the microcells with an internal width of 2 and 10 mm were used respectively. X-ray diffraction was recorded using DRON-6 diffractometer. The course of the reactions was monitored by TLC on Silufol UV-254 plates (eluent: *n*-hexane:acetone, 3:1) and development with I_2 or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography.

The differential scanning calorimetry (DSC) measurements were recorded on a Mettler DSC 30 calorimeter at a scan rate of 10 K/min.

The ionisation potential I_p was measured by the electron photoemission in air method as described in ref [9]. The samples for the ionisation potential measurement were prepared by dissolving materials in THF and were coated on Al plates pre-coated with $\sim 0.5\,\mu m$ thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5–1 μm.

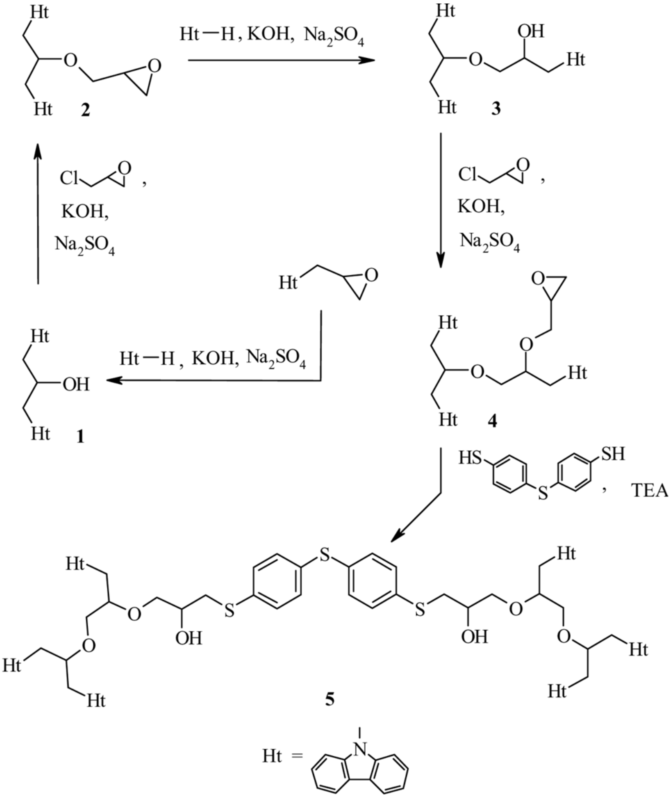
The hole drift mobility was measured by time-of-flight technique [10].

RESULTS AND DISCUSSION

We have synthesized the compound **5** by five-step synthetic route as shown in Scheme 1. The first and the third steps were nucleophilic oxirane ring opening reactions of EPC and 1,3-di(carbazol-9-yl)-2-propanol glycidyl ether (**2**) with carbazole in the presence of KOH and Na_2SO_4. Glycidyl ethers **2** and **4** were prepared in the second and fourth steps by interaction 1,3-di(carbazol-9-yl)-2-propanol (**1**) and 1,6-di(carbazol-9-yl)-5-(carbazol-9-methyl)-4-oxa-2-hexanol (**3**) with CEP in the presence of KOH and Na_2SO_4. In the final step two molecules of glycidyl ether **4** were linked by the nucleophilic opening of the oxirane cycle with 4,4′-thiobisbenzenethiol in the presence of catalyst TEA. The resulting product was purified by column chromatography.

All synthetic steps are facile and easily controlled. The synthesized compounds are soluble in common organic solvents, such as THF, acetone, MEK, toluene at room temperature. The structure of **1–5** was identified by mass, IR, and ^{1}H NMR spectroscopy. The data were found to be in agreement with the proposed structures.

The thermal investigation of **5** was performed by DSC (Fig. 1). The glass transition temperature (T_g) of **5** was observed at 72°C during the second heating, and no peaks due to crystallization and melting were observed, this means that the original state of the sample is amorphous



SCHEME 1 Synthesis of materials under study.

above room temperature. All our attempts to crystallise **5** were unsuccessful. The use of more branched glycidyl ether **4** instead of **2** lenghthens the aliphatic chain, increases number of branches and decreases T_g from 90°C [8] to 72°C.

The amorphous state of **5** was confirmed by X-ray diffraction measurment too (Fig. 2).

X-ray diffraction patterns show only broad halo. Such high morphological stability of this glass can apparently be explained by the flexibility of aliphatic linking chain.

Compounds **4** and **5** were investigated as charge transporting material (CTM). Since π-electrons are very important for the charge transporting process in the TM structures, the absorption spectra of dilute THF solutions of **3**, **5** and EPC are given in Figure 3. All compounds absorb light in the region of 220–350 nm. The light absorption

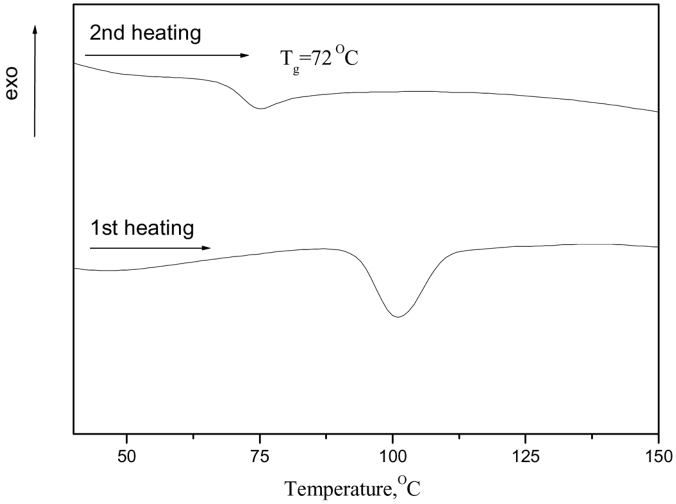


FIGURE 1 DSC curves of **5**; heating rate 10°C/min.

spectra of the molecular glasses **3**, **5** are very similar to that of EPC and show bands typical to N-substituted carbazolyl chromophore due to $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The comparison of UV spectra

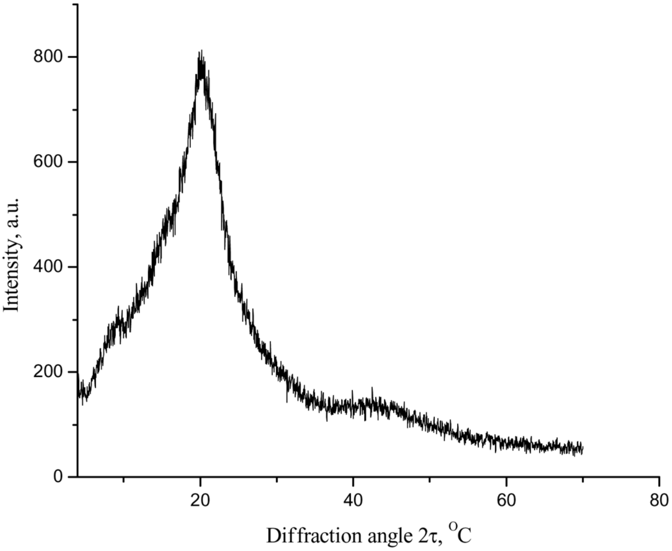


FIGURE 2 Radiograph of molecular glass **5**.

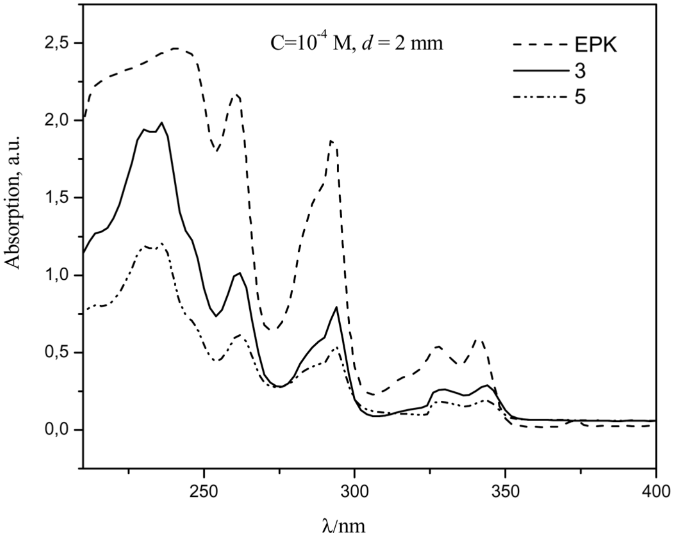


FIGURE 3 UV absorption spectra of the dilute THF solutions (10^{-4} M) of compounds **3**, **5** and EPC.

of compounds containing one (EPC), three (**3**) and six (**5**) carbazolyl moieties showed, that increasing number of carbazolyl chromophores led to a noticeable hipochromic shift.

All these compounds possess fluorescence properties. For the illustration fluorescence spectra of dilute solution of **3**, **5** and EPC are presented in Figure 4. The fluorescence intensity of compounds **3**, **5** is very similar to that of EPC.

The fluorescence maximum of **3** and **5** are at 367 nm and 365 nm respectively, meanwhile the maximum of EPC is at 362 nm.

Amorphous thin films from **5** on substrate were prepared by the casting technique [9]. The ionization potential value for compound **5** is 5.92 eV and is sufficient for use this compound as CTM.

The hole drift mobility, measured by the time-of-flight technique, in the amorphous film of **5** reaches 10^{-5} cm^2 V^{-1} s^{-1} at an electric field of 10^6 V cm^{-1}. This is rather high mobility keeping in mind that carbazole chromophores are electronically isolated in these molecules. Such or even lower hole mobilities have been observed in many molecular glasses consisting of π-conjugated molecules. The morphological stability of **5** allowed the preparation of amorphous film in the organic photoreceptors without binder materials. Figure 5 shows the electric field dependences of the hole drift mobility of the amorphous film of **5**.

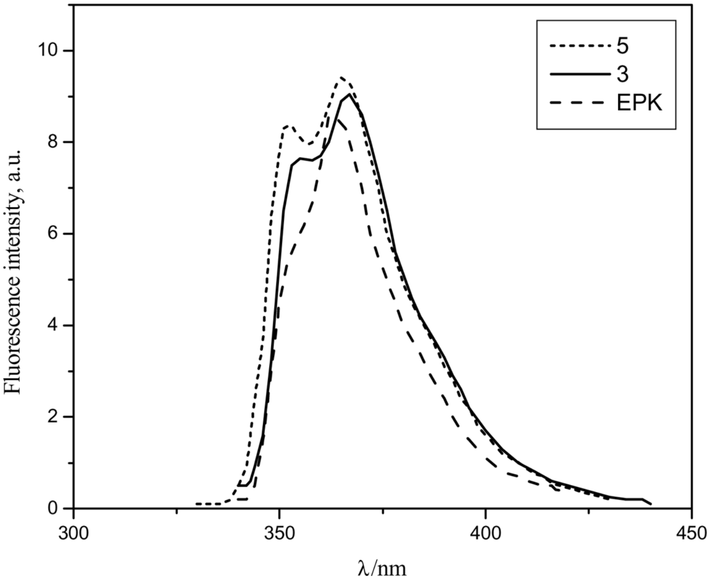


FIGURE 4 Fluorescence spectra of the dilute THF solutions (10^{-4} M) of compounds **3**, **5** and EPC ($\lambda_{\text{ex}} = 310\,\text{nm}$).

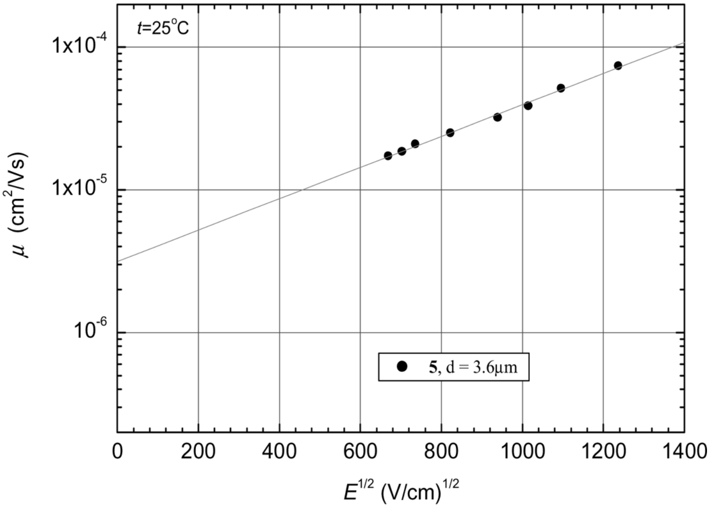


FIGURE 5 Field dependencies of the hole drift mobility in neat layers of molecular glass **5**.

CONCLUSIONS

Hole-transporting six carbazolyl chromophores containing branched molecular glass have been synthesized and its optical, thermal and photoelectrical properties have been studied. Molecular glass **5** absorb light in the range of 220–350 nm. Its glass transition temperature ($T_g = 72°C$), ionization potential (5.92 eV) and hole drift mobility exceed ($10^{-5}\,cm^2/V \cdot s$ at an electric field of $10^6\,V \cdot cm^{-1}$) are reported.

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