



Hole-transporting glass-forming indolo[3,2-*b*]carbazole-based diepoxy monomer and polymers

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ABSTRACT

Hole-transporting indolo[3,2-*b*]carbazole-based diepoxy monomer and polymers are reported. The polymers were prepared by polyaddition reaction of indolo[3,2-*b*]carbazole diepoxide with aromatic dithiols in the presence of triethylamine. Their number average molecular weights range from 11500 to 14310 and polydispersity indices are in the range of 2.96–3.08. Thermal, optical, photophysical, electrochemical and photoelectrical properties of the title compounds were studied. Both the monomer, 5,11-di-2,3-epoxypropyl-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole and the polymers were found to form glasses with the glass transition temperatures ranging from 37 °C for the monomer to 99 °C for one of the polymers. Time-of-flight hole drift mobilities observed in the solid amorphous films of the monomer exceeded $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at an electric field of 10^6 V cm^{-1} .

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1. Introduction

Over the past decade, electroactive molecules have been applied as active components in optoelectronic and electronic devices such as light emitting diodes [1], field effect transistors [2], photovoltaic cells [3], electrophotographic photoreceptors [4]. Organic electroactive materials are very attractive due to their good processability, low cost, and tunable electrical as well as optical properties through structure modification [5,6]. However, stability and processability together with good charge transport properties are still important problems which have to be solved. For this reason the search for new interesting electrophores is constantly pursued in many laboratories. Recently, different indolocarbazoles have been widely studied mainly as effective charge-transporting materials. In 1999, Hu et al. [7] reported the first electroactive indolo[3,2-*b*]carbazole derivative, 5,11-dihydro-5,11-di-1-naphthylindolo[3,2-*b*]carbazole that showed an unusual atropisomerism and excellent hole-

transport properties in organic light emitting diodes. In 2004, Wakim et al. [8] successfully fabricated organic field-effect transistor using 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole as an active layer. Later, Wu et al. [9] reported on fabrication of high-mobility organic thin-film transistors using *N,N*-disubstituted indolo[3,2-*b*]carbazoles as *p*-channel semiconductors. Indolocarbazole-based polymers, i.e. polyindolocarbazoles, polydiindolocarbazoles and poly(indolo-carbazole-alt-bithiophene)s have also been reported and their optical, electrochemical, magnetic and conductive properties have been studied [10]. In this article we report on the synthesis of new indolo[3,2-*b*]carbazole-based diepoxy monomer and demonstrate the possibilities to prepare hole-transporting polymers from the newly synthesized monomer.

2. Experimental

2.1. Materials

The starting compounds, i.e. 1*H*-indole, 2-(chloromethyl)oxirane, *n*-hexanal, triethyl orthoformate, methane-

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sulfonic acid, benzene-1,3-dithiol, 4,4'-thiobisbenzenethiol, triethylamine (TEA) were purchased from Aldrich and used as received. The required chemicals, i.e. iodine, potassium hydroxide, tetrabutylammonium hydrogen sulphate (TBAS), sodium sulphate, sodium sulfite were also purchased from Aldrich. Organic solvents were purified and dried by standard methods [11]. Silica gel was used for column chromatography.

6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole was prepared by the earlier reported procedure [12].

2.1.1. 5,11-Di-2,3-epoxypropyl-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**1**)

6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (2 g, 6.13 mmol) and TBAS (0.02 g, 0.06 mmol) were dissolved in 15 ml of 2-(chloromethyl)oxirane and 8 ml of dry tetrahydrofuran (THF). Then powdered potassium hydroxide (1.71 g, 30.65 mmol) and sodium sulphate (0.69 g, 4.90 mmol) were added in small portions. The reaction mixture was heated at 65 °C for 4 h. The inorganic components were removed by filtration and the excess of oxirane and THF was removed by distillation under reduced pressure. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (1:4, v/v) as an eluent and recrystallized from methanol. The product was obtained as pale yellow crystals (2.28 g, 85% yield) mp: 136–137 °C. FW = 438.57 g mol⁻¹. MS (APCI⁺, 20 V), *m/z* (%) = 439 ([M+H]⁺, 382). IR (in KBr) ν cm⁻¹: 3048 (CH_{ar}), 2870 (CH_{aliphatic}), 1479, 1464 (C=C_{ar}), 1333 (C-N), 1225 (C-O-C); γ cm⁻¹: 740 (CH_{ar}). ¹H NMR (300 MHz, CDCl₃) 0.98 (t, **3H**, -CH₃, *J* = 7.32 Hz), 1.42–1.54 (m, **2H**, -CH₂CH₃), 1.64–1.74 (m, **2H**, -CH₂CH₂CH₃), 1.79–1.99 (m, **2H**, -CH₂-CH₂-CH₂-CH₃), 2.67–2.70 (dd, **2H**, (H_B), *J*_{BX} = 2.56 Hz, one of CH₂O protons), 2.79–2.84 (dd, **2H**, (H_A), *J*_{AX} = 4.02 Hz, *J*_{AB} = 4.76 Hz, another of CH₂O protons), 3.39–3.43 (m, **1H**, CHO), 3.48–3.52 (m, **1H**, CHO), 3.65–3.70 (t, **2H**, -CH₂-CH₂-CH₂-CH₂-CH₃, *J* = 7.68 Hz), 4.53–4.66 (m, **2H**, one of NCH₂ protons), 4.84–5.03 (m, **2H**, another of NCH₂ protons), 7.21–7.29 (m, **2H**, 2 ICZ-H), 7.44–7.51 (m, **2H**, 2 ICZ-H), 7.59–7.62 (d, **1H**, *J* = 8.42 Hz, 1 ICZ-H), 7.67–7.70 (d, **1H**, *J* = 8.05 Hz, 1 ICZ-H), 8.17–8.19 (d, **1H**, *J* = 8.05 Hz, 1 ICZ-H), 8.24–8.27 (d, **1H**, *J* = 7.68 Hz, 1 ICZ-H), 8.33 (s, **1H**, ICZ-H12). Anal. Calcd. for C₂₉H₃₀N₂O₂: C, 79.42; H, 6.89; N, 6.39; O, 7.30. Found: C, 79.88; H, 6.43; N, 6.42; O, 7.27.

Polymers **2–3** were prepared according to the general procedure described below. 1.14 mmol of the monomer **1**, 1.14 mmol of 4,4'-thiobisbenzenethiol (for the synthesis of polymer **2**) or 1.14 mmol of benzene-1,3-dithiol (for the synthesis of polymer **3**) and 0.16 ml (1.1 mmol) of TEA were refluxed in 15 ml of THF under N₂ atmosphere for 60 h. The reaction mixture was cooled down to the room temperature and filtered through 4–6 cm layer of silica gel which then was washed with THF. The obtained solution was concentrated to 15 ml by evaporation and then poured into 20-fold excess of methanol with intensive stirring. The resulting precipitate was filtered off, washed with methanol. Both polymers were Soxhlet extracted with acetone to remove low molecular weight fractions, dissolved

in THF and reprecipitated in methanol. The yields of polymers **2** and **3** were 60 and 70%, respectively.

2.1.2. Polymer (**2**)

¹H NMR (300 MHz, CDCl₃) 0.79–0.90 (m, **3H**, -CH₃), 1.28–1.41 (m, **2H**, -CH₂CH₃), 1.50–1.85 (m, **4H**, -CH₂CH₂-CH₂-CH₃), 3.02–3.24 (m, **4H**, CH₂S), 3.46–3.61 (m, **3H**, CH₂CH), 4.13–4.24 (m, **2H**, -CH₂-CH₂-CH₂-CH₂-CH₃), 4.41–4.71 (m, **4H**, CH₂CH and OH), 5.46–5.55 (m, **1H**, OH), 7.01–7.26 (m, **10H**, 2 ICZ-H and **8H** of benzene ring), 7.32–7.42 (m, **2H**, 2 ICZ-H), 7.52–7.62 (m, **2H**, 2 ICZ-H), 8.05–8.18 (m, **3H**, 3 ICZ-H). IR (in KBr) ν cm⁻¹: 3350 (OH, broad), 3048 (CH_{ar}), 2948 (CH_{aliphatic}), 1479, 1464 (C=C_{ar}), 1333 (C-N), 635, 617 (C-S); γ cm⁻¹: 740 (CH_{ar}).

2.1.3. Polymer (**3**)

¹H NMR (300 MHz, CDCl₃) 0.77–0.91 (m, **3H**, -CH₃), 1.23–1.42 (m, **2H**, -CH₂CH₃), 1.48–1.91 (m, **4H**, -CH₂CH₂-CH₂-CH₃), 3.06–3.26 (m, **4H**, CH₂S), 3.46–3.61 (m, **3H**, CH₂CH), 4.11–4.25 (m, **2H**, -CH₂-CH₂-CH₂-CH₂-CH₃), 4.11–4.66 (m, **4H**, CH₂CH and OH), 5.40–5.56 (m, **1H**, OH), 6.96–7.20 (m, **5H**, 2 ICZ-H and **3H** of benzene ring), 7.28–7.42 (m, **3H**, 2 ICZ-H and **1H** of benzene ring), 7.48–7.61 (m, **2H**, 2 ICZ-H), 8.01–8.12 (m, **3H**, 3 ICZ-H). IR (in KBr) ν cm⁻¹: 3353 (OH, broad), 3048 (CH_{ar}), 2950 (CH_{aliphatic}), 1472, 1460 (C=C_{ar}), 1330 (C-N), 634, 619 (C-S); γ cm⁻¹: 740 (CH_{ar}).

2.2. Instrumentation

¹H NMR spectra of the solutions of the synthesized compounds in deuterated solvents were taken on a Varian Unity Inova (300 MHz (¹H)) spectrometer. All the data are given as chemical shifts δ (ppm) downfield from Si(CH₃)₄. IR spectra of the solid compounds in a form of KBr pellets were recorded using Perkin-Elmer Spectrum GX FT-IR spectrometer. Mass spectra were obtained on a Waters ZQ 2000. Elemental analysis was performed with an Exeter Analytical CE-440 Elemental. The average molecular weights and molecular weight distributions were estimated by gel permeation chromatography (GPC) using a Waters GPC system including a Waters 410 UV detector (254 nm) and four columns (300 × 7.5 mm) filled with PL-Gel absorbent (pore sizes: 106, 105, 104 and 5000 nm) using THF as eluent. Polystyrene standards were used for column system calibration.

UV-Vis absorption spectra were recorded using Spectronic Genesys™ 8 UV-Visible spectrometer (spectral slitwidth 2 nm, wavelength accuracy <1 nm). Fluorescence emission and excitation spectra were recorded with a Hitachi MPF-4 (Japan) luminescence spectrometer (emission slitwidth 2 nm). Differential scanning calorimetry (DSC) measurements were carried out with a Perkin-Elmer DSC-7 at 10 °C min⁻¹ heating rate under nitrogen atmosphere. The glass transition temperatures (*T*_g) were determined from the second heating scans. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA852^e at a 10 °C min⁻¹ heating rate under nitrogen atmosphere. The melting point was measured on a Electrothermal MEL-TEMP melting point apparatus.

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