

# Hole transporting 3,4-ethylenedioxythiophene-based hydrazones

Ramunas Lygaitis<sup>a</sup>, Juozas Vidas Grazulevicius<sup>a,\*</sup>, Francois Tran Van<sup>b</sup>,  
Claude Chevrot<sup>b</sup>, Vygintas Jankauskas<sup>c</sup>, Dalia Jankunaite<sup>d</sup>

<sup>a</sup> Department of Organic Technology, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania

<sup>b</sup> Laboratoire de physicochimie des polymères et des interfaces (LPPI), Université de Cergy-Pontoise, Site Neuville II,  
5 Mail Gay-Lussac 95031 Neuville/Oise, France

<sup>c</sup> Department of Solid State Electronics, Vilnius University, Sauletekio Aleja 9, LT-2040 Vilnius, Lithuania

<sup>d</sup> Department of Environmental Engineering, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania

Received 3 June 2005; received in revised form 4 November 2005; accepted 6 November 2005

Available online 15 December 2005

## Abstract

Hole transporting glass-forming low-molar-mass hydrazones containing 3,4-ethylenedioxythiophene moiety were synthesized and characterized by nuclear magnetic resonance, infrared spectroscopy, and mass spectrometry. The thermal, optical and photoelectrical properties of the synthesized compounds are reported. Four synthesized compounds di(4-(((3,4-ethylenedioxythiophene)-2-methylene 1-phenylhydrazino)-2-hydroxypropyl)-thiophenyl)sulphur, 1,3-bis(((3,4-ethylenedioxythiophene)-2-methylene 1-phenylhydrazino)(3-hydroxy)thiabutyl)benzene, 3,4-ethylenedioxythiophene-2-carbaldehyde *N,N*-diphenylhydrazone and 3,4-ethylenedioxythiophene-2-carbaldehyde *N*-(2,3-epoxypropyl)-*N*-phenylhydrazone form glasses with glass transition temperatures of 68, 64, 37 and 26 °C, respectively as established by differential scanning calorimetry. The ionisation potentials of the synthesized compounds measured by electron photoemission technique in air range from 5.45 to 5.6 eV. Hole drift mobilities in the films of the solid solutions of some of the synthesized hydrazones in bisphenol Z polycarbonate measured by the time-of-flight technique exceed  $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at high electric fields.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** 3,4-Ethylenedioxythiophene; Hydrazone; Glass-forming; Hole transport; Ionisation potential

## 1. Introduction

Aromatic hydrazones are widely studied and used as organic hole transport materials for electrophotographic photoreceptors [1,2]. Hole transporting hydrazones are usually prepared by condensation of formyl derivatives of carbazole, triphenylamine and other aromatic amines with aromatic hydrazines. In this presentation, we report on the synthesis of new hole-transporting hydrazones containing 3,4-ethylenedioxythiophene (EDOT) moieties. EDOT is a commercial compound widely used for the synthesis of electroactive polymers [3–7]. Most of the modern organic electrophotographic photoreceptors have a dual-layer configuration. A charge generation layer usually consists of a dye such as titanyl phthalocyanine dispersed in a polymer binder, e.g. poly(vinylbutyral). A charge transport layer is usually prepared

by imbedding an organic hole transport material into a host polymer, e.g. polycarbonate. This layer has to contain a large amount (50% or even more) of the active material to ensure effective charge transport. Introduction of such a large amount of low-molar-mass charge transport compound into a polymer matrix can lead to crystallization. To prevent this problem charge transporting compounds which do not readily crystallize are required. Some of the EDOT-based hydrazones reported in this work are stable in a solid amorphous state and can be used for the preparation of stable electrophotographic photoreceptors.

## 2. Experimental

### 2.1. Materials

EDOT was donated by “Bayer” and used as received without further purification. Epichlorohydrin, *N*-phenylhydrazine, 1,1-diphenylhydrazine hydrochloride, 1-methyl-1-phenylhydrazine, 4,4'-thiobisbenzenethiol, 1,3-benzenedithiol, phospho-

\* Corresponding author. Tel.: +37037 456525; fax: +37037 456525.  
E-mail address: Juozas.Grazulevicius@ktu.lt (J. Grazulevicius).

rous oxychloride were purchased from "Aldrich" and used as received.

### 2.1.1. 3,4-Ethylenedioxythiophene-2-carbaldehyde (**1**)

A solution of EDOT (13.3 g, 0.093 mol) in 100 ml of 1,2-dichloroethane was added to a 250 ml three-neck round bottomed flask equipped with a reflux condenser and a magnetic stirrer. Then, 11 ml of freshly distilled dimethylformamide and 10.5 ml of phosphorous oxychloride were added and the reaction mixture was stirred under reflux for 2 h. After cooling, the solution was poured into 250 ml of aqueous solution of 1 M of sodium acetate and kept under vigorous stirring for 45 min. After extraction of the organic layer the solvent was removed under vacuum by rotary evaporator. The crude product was purified by a silica gel column chromatography using dichloromethane as an eluent and by recrystallization from methanol. The yield of 3,4-ethylenedioxythiophene-2-carbaldehyde was 76% (12.12 g). M.p. 142–142.5 °C. The <sup>1</sup>H NMR spectrum (250 MHz) of the product in DMSO was characterized by the following chemical shifts (δ, ppm): 9.84 (s, 1H, CHO), 6.74 (s, 1H, CH=S), 4.38–4.33 (m, 2H, OCH<sub>2</sub>), 4.31–4.25 (m, 2H, OCH<sub>2</sub>). The infrared absorption spectrum of the product was characterized by the following absorption peaks (KBr window, cm<sup>-1</sup>): 3109 (C–H in Ht); 2956, 2842, 2811 (aliphatic CH); 1650 (C=O); 1492, 1440 (C=C in Ht); 1063, 911 (C–O); 762 (Ht). The mass spectrum of the product was characterized by the following *m/z* peak: 171 (100%, M + 1).

### 2.1.2. 3,4-Ethylenedioxythiophene-2-carbaldehyde *N*-phenylhydrazone (**2a**)

A mixture of 3,4-ethylenedioxythiophene-2-carbaldehyde (5 g, 0.0294 mol) and 120 ml of methanol was added to a 250 ml three-neck round bottomed flask equipped with a reflux condenser and a magnetic stirrer and the mixture was heated to form a solution. The solution was cooled down to room temperature, and a solution of *N*-phenylhydrazine (4.76 g, 0.0441 mol) in 100 ml methanol was added, and the reaction mixture was heated to 65 °C and stirred for ca. 2.5 h. When the starting material 3,4-ethylenedioxythiophene-2-carbaldehyde was completely reacted, the reaction mixture was concentrated by solvent evaporation and then placed into a freezer to facilitate the crystallization of the product. The product was filtered off, washed with a large amount of cold methanol, and dried. The yield of the yellowish crystals was 62% (4.73 g) and had a melting temperature of 136–137 °C. The <sup>1</sup>H NMR spectrum (100 MHz) of the product in CDCl<sub>3</sub> was characterized by the following chemical shifts (δ, ppm): 7.81 (s, 1H, CH=N), 7.4–6.95 (m, 4H, Ar), 6.82 (t, 1H, *J* = 5.3 Hz, 4-H<sub>Ph</sub>), 6.26 (s, 1H, CH=S), and 4.4–4.1 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>). The infrared absorption spectrum of compound **2a** was characterized by the following absorption peaks (KBr window, cm<sup>-1</sup>): 3317 (N–H); 3115, 3026 (arene C–H); 2990, 2925, 2872 (aliphatic CH); 1600, 1524, 1484, 1456 (C=C in Ar, C=N); 1144, 1063 (C–O); 745 (Ar). The mass spectrum of the product was characterized by the following *m/z* peak: 261 (100%, M + 1).

### 2.1.3. 3,4-ethylenedioxythiophene-2-carbaldehyde *N*-methyl-*N*-phenylhydrazone (**2b**)

A mixture of 3,4-ethylenedioxythiophene-2-carbaldehyde (0.5 g, 0.0294 mol) and 120 ml of methanol was added to a 250 ml three-neck round bottomed flask equipped with a reflux condenser and a magnetic stirrer and the mixture was heated to form a solution. Then the mixture was cooled to the room temperature and a solution of 1-methyl-1-phenylhydrazine (1.0 g, 0.006 mol) in methanol was added dropwise. The reaction mixture was refluxed for 4 h. Then the reaction mixture was cooled down to room temperature and the precipitated product was collected by filtration. The product was purified by column chromatography with an eluent mixture of hexane and diethyl ether in a volume ratio of 1:1. The product was recrystallized from methanol to form yellow crystals. The yield of compound **2b** was 17% (0.14 g). M. p. 132–132.5 °C. The <sup>1</sup>H NMR spectrum (100 MHz) of the product in CDCl<sub>3</sub> was characterized by the following chemical shifts (δ, ppm): 7.59 (s, 1H, CH=N); 7.28 (d, *J* = 4.2 Hz, 4H, 2-H<sub>Ph</sub>, 3-H<sub>Ph</sub>); 7.05–6.75 (m, 1H, 4-H<sub>Ph</sub>); 6.2 (s, 1H, CHS); 4.2 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>); 4.15 (s, 3H, CH<sub>3</sub>N). The infrared absorption spectrum of synthesized compound was characterized by the following absorptions (KBr window, cm<sup>-1</sup>): 3109 (arene C–H); 2970, 2920, 2871 (aliphatic CH); 1597, 1496 (C=C in Ar); 749 (Ar). The mass spectrum of the product was characterized by the following *m/z* peak: 275 (100%, M + 1).

### 2.1.4. 3,4-ethylenedioxythiophene-2-carbaldehyde *N,N*-diphenylhydrazone (**2c**)

Sodium acetate trihydrate (0.88 g, 0.01 mol) was added to a flask equipped with a magnetic stirrer containing a solution of 1.56 g (0.0071 mol) 1,1-diphenylhydrazine hydrochloride in 20 ml of methanol at the room temperature. A solution of 3,4-ethylenedioxythiophene-2-carbaldehyde (0.93 g, 0.0055 mol) in 30 ml of tetrahydrofuran was added dropwise over a period of 15 min. After stirring for 1.5 h at the room temperature, the solvents were removed. The product was extracted with dichloromethane, washed with distilled water, and dried over MgSO<sub>4</sub>. The solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography with an eluent mixture of hexane and diethyl ether in a volume ratio of 1:2. The product was recrystallized from methanol to form yellow crystals. M.p. 161.5–162 °C. The yield of 3,4-ethylenedioxythiophene-2-carbaldehyde *N,N*-diphenylhydrazone was 69% (1.26 g). The <sup>1</sup>H NMR spectrum (100 MHz) of the product in CDCl<sub>3</sub> was characterized by the following chemical shifts (δ, ppm): 7.55–7.0 (m, 11H, Ar, CH=N); 6.22 (s, 1H, CHS); 4.09 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>). The infrared absorption spectrum of compound **3** was characterized by the following absorption peaks (KBr window, cm<sup>-1</sup>): 3058 (arene C–H); 2976, 2922, 2869 (aliphatic CH); 1597, 1588, 1494, 1440 (C=C in Ar, C=N); 1085, 1065, 951 (C–O); 749 (Ar). The mass spectrum of the product was characterized by the following *m/z* peak: 337 (100%, M + 1).

Download English Version:

<https://daneshyari.com/en/article/29117>

Download Persian Version:

<https://daneshyari.com/article/29117>

[Daneshyari.com](https://daneshyari.com)