

Hole transporting 3,4-ethylenedioxythiophene-based hydrazones

Ramunas Lygaitis^a, Juozas Vidas Grazulevicius^{a,*}, Francois Tran Van^b,
Claude Chevrot^b, Vygintas Jankauskas^c, Dalia Jankunaite^d

^a Department of Organic Technology, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania

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

^c Department of Solid State Electronics, Vilnius University, Sauletekio Aleja 9, LT-2040 Vilnius, Lithuania

^d Department of Environmental Engineering, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania

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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.

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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 ¹H 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, OCH₂), 4.31–4.25 (m, 2H, OCH₂). The infrared absorption spectrum of the product was characterized by the following absorption peaks (KBr window, cm⁻¹): 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 ¹H NMR spectrum (100 MHz) of the product in CDCl₃ 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_{Ph}), 6.26 (s, 1H, CH=S), and 4.4–4.1 (m, 4H, OCH₂CH₂). The infrared absorption spectrum of compound **2a** was characterized by the following absorption peaks (KBr window, cm⁻¹): 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 ¹H NMR spectrum (100 MHz) of the product in CDCl₃ 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_{Ph}, 3-H_{Ph}); 7.05–6.75 (m, 1H, 4-H_{Ph}); 6.2 (s, 1H, CHS); 4.2 (s, 4H, OCH₂CH₂); 4.15 (s, 3H, CH₃N). The infrared absorption spectrum of synthesized compound was characterized by the following absorptions (KBr window, cm⁻¹): 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 MgSO₄. 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 ¹H NMR spectrum (100 MHz) of the product in CDCl₃ 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, OCH₂CH₂). The infrared absorption spectrum of compound **3** was characterized by the following absorption peaks (KBr window, cm⁻¹): 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).

2.1.5. 3,4-ethylenedioxythiophene-2-carbaldehyde *N*-(2,3-epoxypropyl)-*N*-phenylhydrazone (**3**)

A mixture of 3,4-ethylenedioxythiophene-2-carbaldehyde *N*-phenylhydrazone (4.6 g, 0.0097 mol) and 24.5 g of epichlorohydrin were added to a 100 ml three-neck round bottomed flask equipped with a reflux condenser and a magnetic stirrer. Potassium hydroxide (3.8 g, 0.068 mol) was added to the reaction mixture in five portions over the course of the reaction. Additionally, 0.25 g of sodium sulphate was added to the flask prior to every addition of potassium hydroxide. The reaction mixture was stirred for 15 h at the room temperature and then filtered off. Epichlorohydrin was removed by vacuum distillation. The crude product was purified by a silica gel column chromatography with a mixture of ethyl acetate and *n*-hexane in a volume ratio of 1:2 as an eluent. The product was recrystallized from diethyl ether to form yellowish crystals. M.p. 107–108 °C The yield of compound **3** was 58% (1.76 g). The ¹H NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 7.79 (s, 1H, CH=N), 7.5–7.25 (m, 4H, Ar), 7.05–6.8 (m, 1H, 4-HPh), 6.23 (s, 1H, CH=S), 4.43–4.27 (dd, 1H, one of NCH₂ protons, (H_A), *J*_{AX} = 2.9 Hz, *J*_{AB} = 9.7 Hz), 4.1–3.78 (dd, 1H, another NCH₂ proton, (H_B), *J*_{BX} = 4 Hz), 3.24 (m, 1H, CH), 2.87 (t, one of OCH₂ protons, (H_B), *J*_{BX} = 4.2 Hz), and 2.7–2.55 (dd, 1H, CH₂O another proton, (H_A), *J*_{AX} = 2.7 Hz). The infrared absorption spectrum of compound **3** was characterized by the following absorption peaks (KBr window, cm⁻¹): 3124, 3058 (arene C–H); 2976, 2922, 2869 (aliphatic CH); 1595, 1500, 1442 (C=C in Ar, C=N); 1069, 935, 907 (C–O); 760 (Ar). The mass spectrum of the product was characterized by the following *m/z* peak: 317 (100%, M + 1).

2.1.6. Di(4-(((3,4-ethylenedioxythiophene)-2-methylene 1-phenylhydrazino)-2-hydroxypropyl)-thiophenyl)sulphur (**4a**)

Three drops of triethylamine (TEA) were slowly added to the solution of 0.7 g (2.2 mmol) of 3,4-ethylenedioxythiophene-2-carbaldehyde *N*-(2,3-epoxypropyl)-*N*-phenylhydrazone and 0.26 g (1.0 mmol) of 4,4'-thiobisbenzenethiol in 10 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30 °C. The reaction mixture was kept overnight at the room temperature. After the evaporation of the solvent, the residue was purified by a silica gel column using ethyl acetate and *n*-hexane in a volume ratio of 1:4 as an eluent. The yield of the yellow amorphous product was 0.64 g (73%). The ¹H NMR spectrum (250 MHz) of the product in d₆-DMSO was characterized by the following chemical shifts (δ, ppm): 7.94 (s, 2H, CH=N), 7.4–7.16 (m, 16H, Ar), 6.82 (t, 2H, *J* = 6.9 Hz, 4-HPh), 6.49 (s, 2H, CH=S), 5.56 (d, 2H, *J* = 3.2 Hz, OH), 4.26–4.14 (m, 8H, OCH₂CH₂), 4.12–3.9 (m, 6H, CHOH, NCH₂CH), and 3.28–3.04 (m, 4H, CH₂S). The infrared absorption spectrum of compound **4a** was characterized by the following absorption peaks (KBr window, cm⁻¹): 3426 (OH), 3105 (arene C–H), 2977, 2921, 2870, (aliphatic C–H), 1596, 1515, 1439 (Ar C=C), and 1146 (C–N). The mass spectrum of the product was characterized by the following *m/z* peak: 884 (M + 1).

2.1.7. 1,3-bis(((3,4-ethylenedioxythiophene)-2-methylene 1-phenylhydrazino)(3-hydroxythiabutyl)benzene (**4b**)

Three drops of triethylamine were slowly added to a solution of 0.81 g (2.56 mmol) of 3,4-ethylenedioxythiophene-2-carbaldehyde *N*-(2,3-epoxypropyl)-*N*-phenylhydrazone and 0.158 g (1.13 mmol) of 1,3-benzenedithiol in 15 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30 °C. The reaction mixture was kept overnight at room temperature. After the evaporation of the solvent, the residue was subjected to column chromatography using ethyl acetate and *n*-hexane in a volume ratio of 1:4 as an eluent. The yield of the yellow amorphous product was 0.69 g (81%). The ¹H NMR spectrum (250 MHz) of the product in d₆-DMSO was characterized by the following chemical shifts (δ, ppm): 7.96 (s, 2H, CH=N), 7.39–7.14 (m, 8H, Ar), 6.79 (t, 2H, *J* = 6.9 Hz, 4-HPh), 6.47 (s, 2H, CH=S), 5.56 (s (br), 2H, OH), 4.21 (dd, 8H, OCH₂CH₂), 4.1–3.89 (m, 6H, NCH₂CH), 3.24–3.05 (m, 4H, CH₂S). The infrared absorption spectrum of compound **4b** was characterized by the following absorption peaks (KBr window, cm⁻¹): 3424 (OH), 3103 (arene C–H), 2976, 2920, 2869 (aliphatic C–H), 1595, 1569, 1492, 1438 (Ar C=C), and 1145 (C–N). The mass spectrum of the product was characterized by the following *m/z* peak: 776 (M + 1).

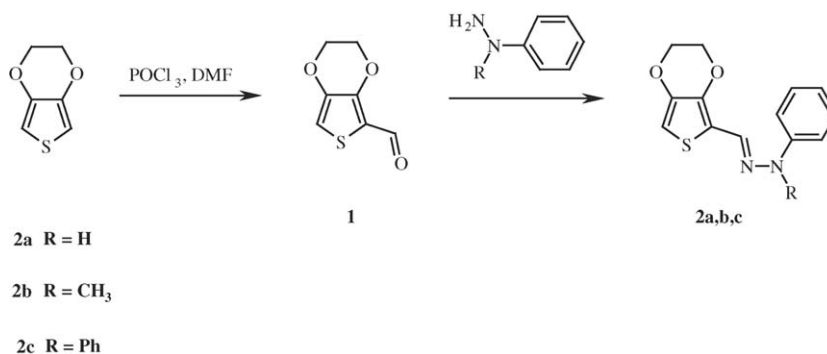
2.2. Methods

¹H NMR spectra were obtained on Bruker AC 250 (250 MHz) and JOEL JNM-FX 100 (100 MHz) instruments. Mass spectra were obtained on a Waters ZQ (Waters, Milford, USA). IR-spectroscopy was performed on Perkin-Elmer 1330 IR, using KBr pellets. UV-vis spectra were recorded with Hitachi Spectronic Unicam GenesysTM 8 spectrophotometer. Fluorescence emission and excitation spectra were recorded with a Hitachi MPF-4 (Japan) luminescence spectrometer. Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC-7 (heating/cooling rate 10 K/min). Thermogravimetric analysis (TGA) was fulfilled using NETZSCH STA 409 thermogravimeter at a heating rate 10 K/min under N₂. Melting points were measured on a Buchi 510 melting point apparatus. The ionisation potentials (*I*_p) of the films of the synthesized compounds were measured by the electron photoemission in air method as described [8,9]. The standard error in the mean to 95% confidence for the values of ionisation potential was 0.04 eV. Hole drift mobilities were measured by a xerographic time-of-flight method [10].

3. Results and discussion

3,4-Ethylenedioxythiophene 1-carbaldehyde hydrazones **2a**, **2b** and **2c** were synthesized by two-step synthetic route, as shown in Scheme 1. The first step was formylation of 3,4-ethylenedioxythiophene by the Vilsmeier method [11] to get formyl derivative **1** in 76 % yield. The second step was condensation of aldehyde **1** with differently substituted hydrazines.

The hydrazone dimers containing EDOT moiety (**4a**, **4b**) were prepared by the two-step synthetic route, shown in Scheme 2. In the first step 3,4-ethylenedioxythiophene 1-

Scheme 1. Synthetic route to compounds **1**, **2a**, **2b** and **2c**.

carbaldehyde *N*-phenylhydrazone was subjected to the action of epichlorohydrin in the presence of KOH to yield oxirane **3**. The nucleophilic reaction of oxirane **3** with 4,4'-thiobisbenzenethiol and 1,3-benzenedithiol at the room temperature in 2-butanone in the presence of TEA gave compounds **4a** and **4b**, respectively. All the synthesized compounds are soluble in common organic solvents such as chloroform, acetone, tetrahydrofuran (THF). The structures of all compounds were confirmed by ¹H NMR, IR spectroscopies and mass spectrometry.

Thermal properties of the synthesized compounds were examined by DSC and TGA. The data obtained are presented in Table 1. The thermal stability of the compounds synthesized are similar to that of other aromatic hydrazones [12,13]. The 5% weight loss temperatures ($T_{\text{dec-5\%}}$) for 3,4-ethylenedioxythiophene-based hydrazones **2b** and **2c** are close to those observed for hydrazone dimers **4a** and **4b** and are in the range 257–274 °C. The lowest 5% weight loss temperature was observed for hydrazone **3** containing reactive epoxy group. All

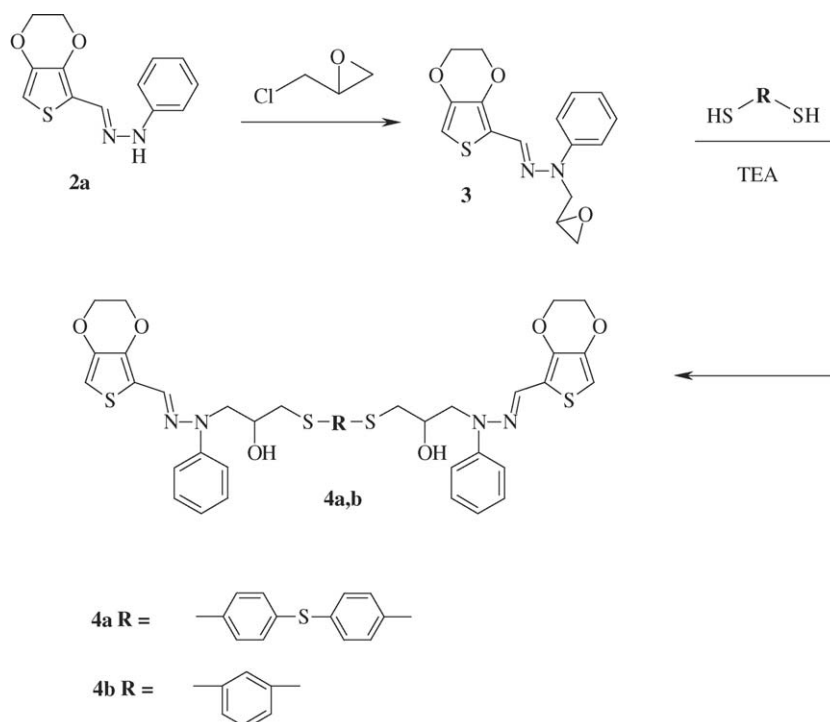
Table 1

Thermal characteristics of the synthesized compounds

Compound	T_g (°C) (2nd heat)	T_m (°C)	T_{cr} (°C)	$T_{\text{dec-5\%}}$ (°C)
2b	–	137	102	262
2c	37	172 ^a	–	257
3	26	112 ^a	–	237
4a	68	–	–	263
4b	64	–	–	274

^a Observed only at the first heating scan.

synthesized EDOT-based compounds except **2b** form molecular glasses. The first DSC runs of hydrazones **2c** and **3** reveal melting at 172 and 112 °C but after slow cooling, the second heating runs reveal only glass transitions at 37 and 26 °C, respectively. Hydrazone having methyl substituent (**2b**) shows crystallization and a following melting in the second DSC heating-cooling cycle and no glass transition was observed. Compound **4a** shows a similar behaviour to that of **4b**, i.e., only glass transition temperatures

Scheme 2. Synthetic route to compounds **3**, **4a** and **4b**.

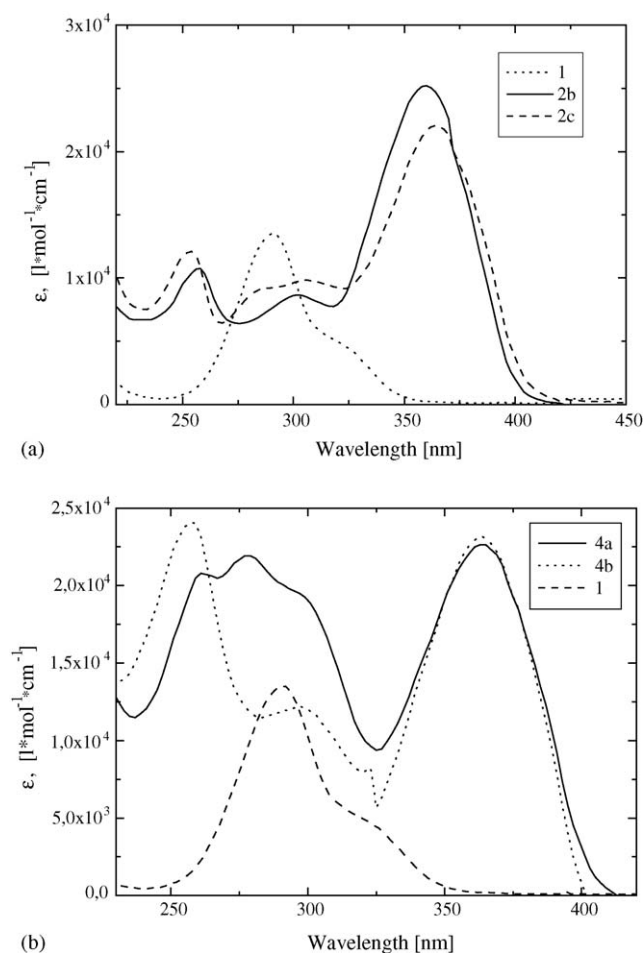


Fig. 1. UV-vis absorption spectra of the dilute THF solutions of compounds **1**, **2b**, **2c** (a) and of compounds **1**, **4a**, **4b** (b).

at 68 and at 64 °C, respectively are observed in the repeated DSC runs and no peaks due to crystallization and melting appear.

UV-vis absorption spectra of the dilute solutions of EDOT-based hydrazones are given in Fig. 1. All the synthesized compounds absorb light under 400 nm. The lowest energy absorption band maxima are between 359 and 365 nm for all compounds.

It is obvious that new absorption bands are formed in the spectra of all synthesized materials in comparison with the spectrum of 3,4-ethylenedioxythiophene-2-carbaldehyde. This observation shows that the molecules of the hydrazones and hydrazone dimers are π -conjugated through the lone electron pairs of the nitrogen atoms which extend the delocalization as compared with **1**. The UV spectrum of compound **2c**, containing two phenyl substituents at the nitrogen atom of hydrazone moiety shows bathochromic shift of 5–6 nm with respect of the spectrum of methyl phenyl substituted hydrazone **2b**. The maxima of K bands, attributed to $\pi \rightarrow \pi^*$ transitions of compounds **4a** and **4b** are at the same wavelength (363 nm). The different aromatic linking parts of compounds **4a** and **4b** are electronically isolated, and apparently it does not influence $\pi \rightarrow \pi^*$ transitions. The differences in the UV spectra of hydrazones **4a** and **4b** are observed only in the region of 250–300 nm.

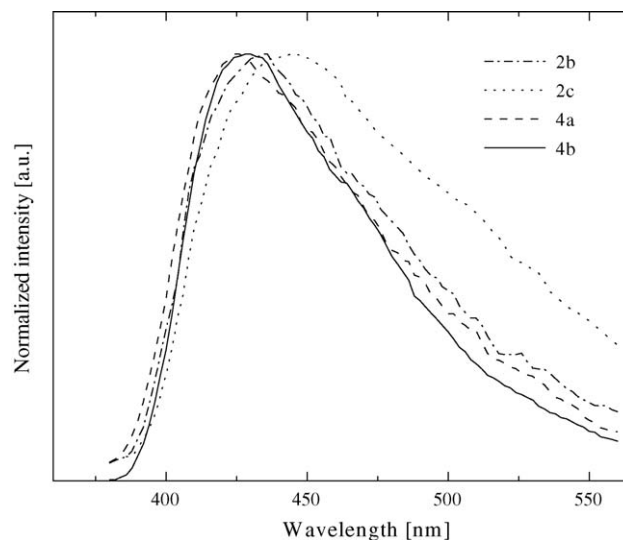


Fig. 2. Fluorescence spectra of dilute THF solutions (10^{-6} M) of compounds **2b**, **2c**, **4a** and **4b** ($\lambda_{\text{ex}} = 320$ nm).

Fig. 2 shows fluorescence spectra of the dilute solutions of compounds **2b**, **2c**, **4a** and **4b**. Blue luminescence peaking in the range 426–444 nm is characteristic of the dilute THF solutions of the synthesized compounds.

The values of I_p are given in Table 2. The I_p value of hydrazone **2c**, having a diphenyl-substituted *N* atom of the hydrazone moiety, is by 0.15 eV lower than that of dihydrazone **2b**, which bear methyl and phenyl substituents at the hydrazone *N* atom. The I_p values of the epoxypropyl substituted hydrazone **3** and of the dimmers **4a** and **4b** are close to that of **2b**. These data correlate with UV-vis absorption and fluorescence spectroscopy data. From the point of the view of I_p values the reported hydrazones are applicable as hole transport materials in electrophotographic photoreceptors. Holes can be easily injected into charge transport layer containing these materials from charge generation layer with ionization potential close to these values. The I_p values for charge generation materials widely used in electrophotographic photoreceptors, such as titanil phthalocyanines [14–16], perylene pigments [17] and bisazo pigments [18] are in the range 5.1–5.6 eV.

Time flight technique was used to study charge transport properties of EDOT-based hydrazones doped in bisphenol Z polycarbonate (PC-Z) (50 wt.%). The linear dependencies of hole drift mobilities μ_h on the square root of electric field was observed for all the systems (Fig. 3). The highest hole mobilities were observed for hydrazones **2b** and **2c** doped PC-Z. The

Table 2
Ionisation potentials of EDOT-based hydrazones

Compound	I_p (eV)
2b	5.6
2c	5.45
3	5.6
4a	5.56
4b	5.54

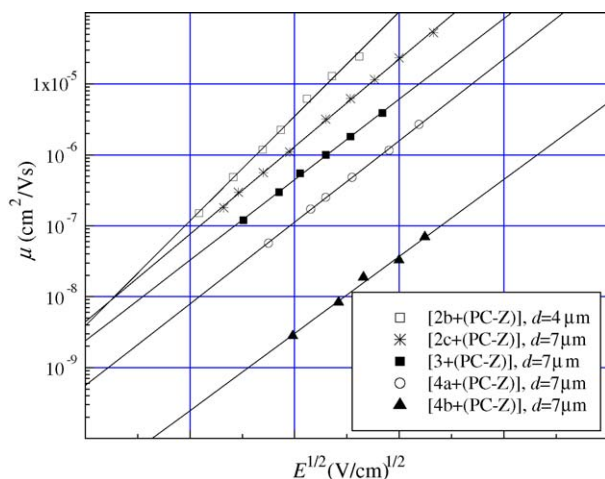


Fig. 3. Electric field dependencies of hole drift mobilities for 50% solid solutions in PC-Z of compounds **2b**, **2c**, **3**, **4a** and **4b**.

hole drift mobility of $2 \times 10^{-5} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$ was observed for the system containing compound **2b** at an electric field strength of $10 \times 10^5 \text{ V cm}^{-1}$ at 293 K. PC-Z doped with EDOT-based hydrazone dimers **4a** and **4b** showed lower hole mobilities than PC-Z doped with hydrazones **2a**, **2b** and **3**. This observation can be explained by the lower electrophore concentration in the dimer molecules and by the presence of hydroxyl groups, which can act as the traps of charge carriers [19].

In conclusion, we have synthesized new hydrazones and hydrazone twin molecules containing 3,4-ethylenedioxythiophene moiety and have determined their optical, thermal and optoelectrical properties. Almost all synthesized compounds form glasses with glass transition temperatures between 26 and 68 °C. The ionisation potentials of the synthesized compounds measured by electron photoemission technique in air range from 5.45 to 5.6 eV. We have studied charge transport properties of 50% solid solutions of the synthesized compounds in bisphenol Z polycarbonate by xerographic time of light technique and observed hole drift mobilities of the order of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at high electric fields.

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