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New Thiophene-Based Glass-Forming Hydrazones for Optoelectronic Applications

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A new series of thiophene-containing glass-forming hydrazones is synthesized. The thermal, photoelectrical, and optical properties of these compounds are examined. The synthesized hydrazones exhibit the thermal stability sufficient for their application in optoelectronic devices. The values of ionization potential of amorphous films of the newly synthesized hydrazones are from 4.43 to 5.79 eV. The hole drift mobilities measured by the xerographic time-of-flight method in a molecularly doped polymer containing 50 wt.% of one synthesized hydrazone exceed 10^{-6} cm^2/Vs at an electric field intensity of 6.4×10^{-5} $V\ cm^{-1}$.

Keywords: hole-drift mobility; hydrazone; ionization potential; thiophene

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INTRODUCTION

Organic charge-transporting materials are used in optoelectronic and electronic devices like electrophotographic photoreceptors, organic light-emitting diodes, photovoltaic cells, field-effect transistors, and other devices [1,2]. Hydrazones play an important role among organic hole transport materials, especially those used in electrophotography, because of their simple synthesis and high charge carrier mobilities [3,4]. Thiophene-based hydrazones are poorly studied up to now and represent a relatively new family of organic hole transport materials [5]. Since the presence of sulphur or oxygen atoms in the molecules of organic semiconductors improves their characteristics [7], we continue the work on the design and synthesis of hole-transporting thiophene-based hydrazones. In this presentation, we report on the synthesis and characterization of new thiophene-based hole-transporting glass-forming hydrazones, containing reactive and polymerizable functional groups. The presence of reactive functional groups in these structures makes them useful for the preparation of polymeric charge-transporting materials.

EXPERIMENTAL

Materials

3,4-ethylendioxythiophene (EDOT), butyllithium (2.5 M solution in hexane), N-phenylhydrazine, 3-(bromomethyl)-3-methyl oxetane, 2-chloroethyl vinyl ether, thiophene-2-carbaldehyde, phosphorus oxychloride, potassium hydroxide, potassium carbonate, tetrabutylammonium hydrogen sulphate, and sodium sulphate were purchased from Aldrich and used as-received. The solvents were purified and dried using standard procedures [8].

2-(formyl)3,4-ethylenedioxythiophene (1a) was synthesized by the Vilsmeier reaction of 3,4-ethylenedioxythiophene with $POCl_3$. The synthesis and characteristics have been already reported in [6].

2-(5-(5-(formyl)thiophene-2-yl)thiophen-2-yl)thiophene (1c) was synthesized by the Vilsmeier formylation method [9]. Yielded (31%). ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 7.01–7.69 (m, 7H, Ar), 9.84 (s, 1H, CHO). MS(APCI$^+$, 20 V), m/z (%): 277 ($[M+H]^+$, 100).

2-(N-phenylhydrazonemethyl)3,4-ethylenedioxythiophene (2a). The characteristics of **2a** have been already reported in [6].

2-(N-phenylhydrazonemethyl)thiophene (2b). Thiophene 2-dicarbaldehyde (2.0 g, 17.83×10^{-3} mol) was dissolved in 60 ml of ethyl alcohol under mild heating. Then, a solution of 3.80 g (35.67×10^{-3} mol of N-phenylhydrazine in 5 ml of ethyl alcohol) was

added. The reaction mixture was refluxed for 1.5 h. The precipitated product was filtered and washed with methyl alcohol and dried. The yield of **2b** was 87% (3.15 g). Yield (87%). FW = 202 g mol^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 6.88–7.62 (m, 8H, Ar), 7.80 (s, 1H, CH=N). MS(APCI$^+$, 20 V), m/z (%): 203 ([M + H]$^+$, 100).

2-(5-(5-(N-phenylhydrazonemethyl)thiophene-2-yl)thiophen-2-yl)thiophene (2c) was synthesized by the same procedure as **2b**. The yield of **2c** was 88%. FW = 366 g mol^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 6.90–7.62 (m, 8H, Ar), 7.82 (s, 1H, CH=N). MS(APCI$^+$, 20 V), m/z (%): 367 ([M + H]$^+$, 100).

2-(N-(3-methyloxetan-3-yl)N-phenylhydrazonemethyl)3,4-ethylenedioxythiophene (3a). 2-(N-phenylhydrazonemethyl)3,4-ethylenedioxythiophene **(2a)** (0.5 g, 1.91×10^{-3} mol) was dissolved in 10 ml of ethyl methyl ketone and 0.6 g (3.82×10^{-3} mol) of 3-(bromomethyl)-3-methyl oxetane and tetrabutylammonium hydrogen sulphate were added. Then 0.32 g (5.73×10^{-3} mol) of KOH and 0.10 g (0.76×10^{-3} mol) of Na_2SO_4 were added by 3 portions. The reaction mixture was refluxed for 15 h. After cooling, the inorganic components were filtered off. The solvent was removed from the filtrate by rotary evaporation. The product was purified by silica gel column chromatography using a mixture of acetone and hexane in a volume ratio of 1:6 as an eluent. The product was crystallized from eluent. Yield 0.28 g (42%) of yellow crystals (mp: 80–81°C), FW = 344 g mol^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 1.55 (s, 3H, CH_3), 3.87 (s, 2H, CH_2), 4.22 (d, 4H, CH_2), 4.32, 4.40 (dd, 2H, CH_2), 4.56, 4.72 (dd, 2H, CH_2), 6.26 (s, 1H, Ar), 7.08 (t, 1H, Ar), 7.27–7.45 (m, 5H, Ar). ^{13}C NMR (250 MHz, $CDCl_3$, δ, ppm): 23.26 (CH_3), 41.43 (C), 56.27 (CH_2–N), 64.98 (CH_2–O), 81.84 (CH_2–O), 99.22 (CH–S), 116.28, 119.42, 123.22, 125.87 (Ar), 129.70 (CH=N, =C–S), 139.87 (N–C=), 141.844, 147.35 (O–C=). IR (KBr), ν/cm^{-1}): 3107, 3026 (C–H in Ar), 2976, 2920, (C–H in Aliphat.), 1635 (C=N), 1599, 1497 (C=C in Ar), 1270 (C–N), 970 (C–S), 755, 698 (C–H in Ar). MS(APCI$^+$, 20 V), m/z (%): 345 ([M + H]$^+$, 100).

2-(N-(3-methyloxetan-3-yl)N-phenylhydrazonemethyl)thiophene (3b) was synthesized by the same procedure as **3a**. Yield 1.52 g (54%) (mp: 78–79°C), FW = 286 g mol^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 1.57 (s, 3H, CH_3), 3.89 (s, 2H, CH_2), 4.35 (d, 2H, CH_2), 4.72 (d, 2H, CH_2), 6.99–7.02 (m, 2H, Ar), 7.13–7.31 (m, 4H, Ar), 7.40–4.47 (m, 3H, Ar). ^{13}C NMR (250 MHz, $CDCl_3$, δ, ppm): 23.20 (CH_3), 41.30 (C), 57.53 (CH_2–N), 81,47 (CH_2–O), 120.88, 125.39, 125.84, 127.43 (Ar), 128.73 (C–S), 129.83 (Ar CH, C–S), 142.43 (CH), 146.90 (C(Ar)–N). IR (KBr, ν/cm^{-1}): 3069, 3025 (C–H in Ar), 2955, 2930, 2868 (C–H in Aliphat.), 1641(C=N), 1595, 1568, 1493, 1465 (C=C in

Ar), 1259 (C–N), 1139 (C–O–C) 976 (C–S), 753, 707, (C–H in Ar). MS(APCI$^+$, 20 V), m/z (%): 287 ([M + H]$^+$, 100).

2-(5-(5-(N-(3-methyloxetan-3-yl)-N-phenylhydrazonemethyl) thiophene-2-yl)thiophen-2-yl)thiophene (3c) was synthesized by the same procedure as **3a**. Yield (40%) of **3c**. FW = 450 g mol^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 1.45 (s, 3H, CH_3), 4.03 (s, 2H, CH_2), 4.11 (d, 2H, CH_2), 4.50 (d, 2H, CH_2), 7.11–7.18 (m, 2H, Ar), 7.28–7.38 (m, 9H, Ar), 7.55 (d, 1H, Ar, CH), 7.79 (s, 1H, Ar). IR (KBr), ν/cm^{-1}): 3065 (C–H in Ar), 2958, 2931 (C–H in Aliphat.), 1665 (C=N), 1596, 1571, 1497, 1462 (C=C in Ar), 1272, 1260 (C–N), 1127 (C–O–C), 977 (C–S), 748, 693 (=C–H). MS(APCI$^+$, 20 V), m/z (%): 451 ([M + H]$^+$, 100).

2-(N-vinyloxyethyl-N-phenylhydrazonemethyl)3,4-ethylene-dioxythiophene (4a). To a 250-ml three-neck round bottom flask equipped with a reflux condenser and a magnetic stirrer, 3,4-ethylene-dioxythiophene-2-carbaldehyde-N-phenylhydrazone (4) (2 g, 7.69×10^{-3} mol) was added and dissolved in 10 ml of ethyl methyl ketone. Then 1.35 ml (15.38×10^{-3} mol) of 2-chloroethyl vinyl ether, 0.86 g (15.38×10^{-3} mol) of KOH and 1.06 g (7.69×10^{-3} mol) of K_2CO_3 were added into the reaction mixture. The reaction mixture was refluxed for 17 h. After cooling, the inorganic components were filtered off. The solvent was removed from the filtrate by rotary evaporation. The product was purified by silicagel column chromatography using a mixture of acetone and hexane in a volume ratio of 1:7 as an eluent. The product was crystallized from the eluent. Yield 1.29 g (50%) of yellow crystals (mp: 79–80°C), FW = 330 g mol^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 3.98 (t, 2H, CH_2), 4.08–4.11 (m, 1H, =CH_2), 4.20–4.31 (m, 7H, CH_2), 6.29 (s, 1H, Ar), 6.50–6.57 (m, 1H, Ar), 6.95–7.00 (m, 1H, Ar), 7.32–7.41 (m, 4H, Ar), 7.80 (s, 1H, Ar). IR (KBr, ν/cm^{-1}): 3106, 3028 (C–H in Ar), 2979, 2921, 2880, (C–H in Aliphat.), 1670(C=N), 1622, 1597, 1497 (C=C in Ar), 1275 (C–N), 1105 (C–O–C), 745, 690 (C–H in Ar). MS(APCI$^+$, 20 V), m/z (%): 331 ([M + H]$^+$, 70).

2-(N-vinyloxyethyl-N-phenylhydrazonemethyl)thiophene (4b) was synthesized by the same procedure as **4a**. Yield (46%) (mp: 74–75°C), FW = 272 g mol^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 3.99 (t, 2H, CH_2), 4.09–4.12 (m, 1H, =CH_2), 4.21–4.28 (m, 3H, CH_2), 6.50–6.57 (m, 1H, Ar), 6.98–7.07 (m, 2H, Ar), 7.16–7.27 (m, 2H, Ar), 7.34–7.44 (m, 4H, Ar), 7.86 (s, 1H, Ar). IR (KBr, ν/cm^{-1}): 3098, 3069, 3042 (C–H in Ar), 2979, 2918, 2878, (C–H in Aliphat.), 1648(C=N), 1594, 1568, 1500, 1478 (C=C in Ar), 1276 (C–N), 1171 (C–O–C), 995 (C–S), 755, 709 (C–H in Ar). MS(APCI$^+$, 20 V), m/z (%): 273 ([M + H]$^+$, 65).

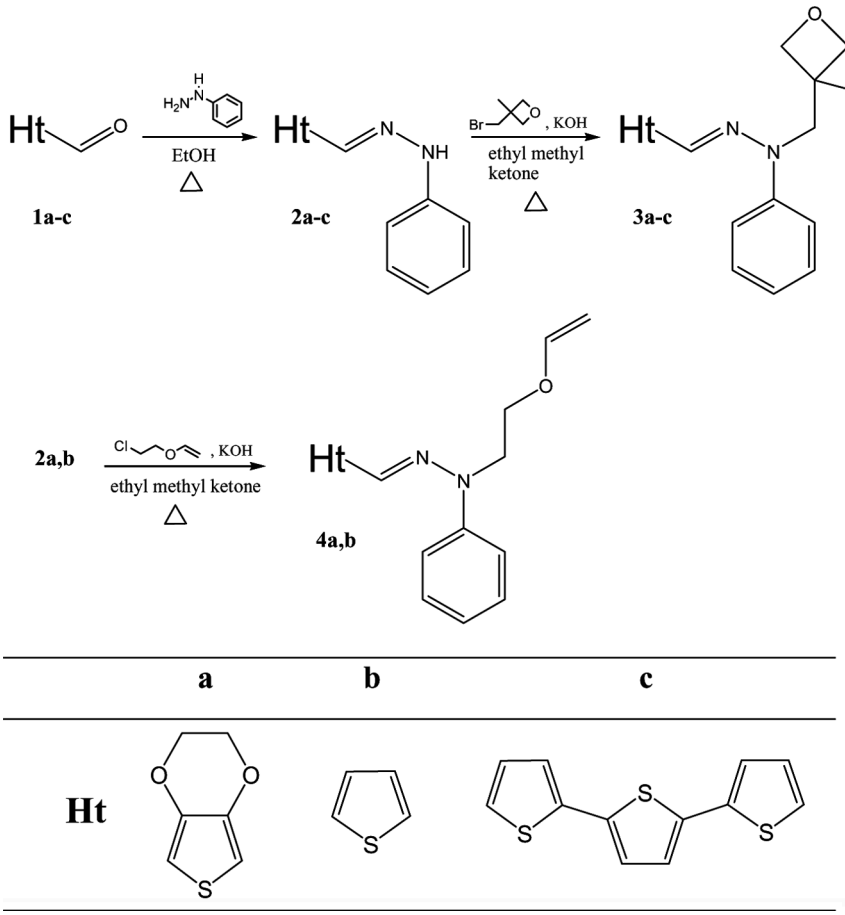
Measurements

The ^{1}H NMR spectra were obtained on Bruker AC 250 (250 MHz) and Bruker DPX 250 (250 MHz) instruments. IR-spectroscopy was performed on a Perkin Elmer Spectrum GX spectrophotometer, using KBr pellets. The mass spectra were obtained on a Waters ZQ 2000. The UV-vis spectra were recorded with a Spectronic Unicam Genesys^{TM} 8 spectrophotometer. The fluorescence emission spectra were recorded with a Hitachi MPF-4 luminescence spectrometer. The differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC-821e at a heating rate of 20°C min^{-1} in the N_2 atmosphere. The thermogravimetric analysis (TGA) was fulfilled using a NETZSCH STA 409 thermogravimeter at a heating rate of 10°C min^{-1} in the N_2 atmosphere.

The ionization potential (I_p) was measured by the method of electron photoemission in air as described before [10]. The samples for the measurements were prepared by casting the solutions of the compounds on Al plates pre-coated with methylmethacrylate and methacrylic acid copolymer as the adhesive layer. The hole drift mobilities of the solid solutions of the synthesized hydrazones in bisphenol Z polycarbonate were measured by the xerographic time-of-flight method [11].

RESULTS AND DISCUSSION

3,4–ethylenedioxythiophene-, thiophene- and terthiophene-based dihydrazones having oxetane and vinyloxyethyl groups were synthesized by the two- or three-step synthetic route as shown in Scheme 1. The first step was the formylation by the Vilsmeier method to produce compound **1a** and **1c**. The second step was the condensation of aldehydes **1a–c** with N-phenylhydrazine to produce compounds **2a–c**. The last step was the alkylation of hydrazones obtained with 3-(bromomethyl)-3-methyl oxetane in the presence of potassium hydroxide to obtain 2-(N-(3-methyloxetan-3-yl)N-phenylhydrazonemethyl)3, 4-ethylenedioxythiophene **3a**, 2-(N-(3-methyloxetan-3-yl)N-phenylhydrazonemethyl)thiophene **3b** and 2-(5-(5-(N-(3-methyloxetan-3-yl)-N-phenylhydrazonemethyl)thiophene-2-yl)thiophen-2-yl)thiophene **3c**. The alkylation with 2-chloroethyl vinyl ether in the presence of potassium hydroxide and potassium carbonate gave 2-(N-vinyloxyethyl-N-phenylhydrazonemethyl)3,4-ethylenedioxythiophene **4a** and 2-(N-vinyloxyethyl-N-phenylhydrazonemethyl)thiophene **4b**. All the final products, i.e., hydrazones **3a–c** and **4a,b**, were purified by column chromatography to obtain pure and well-defined compounds. The



SCHEME 1 Synthesis of compounds **3a–c** and **4a,b**.

structures of the synthesized compounds were confirmed by ^{1}H NMR, IR spectroscopy, and mass spectrometry. Hydrazones **3a–c** and **4a,b** are soluble in common organic solvents such as tetrahydrofuran, chloroform, and acetone.

The signals in the ^{1}H NMR spectra of all the newly synthesized hydrazone compounds can be exactly assigned to the characteristic hydrogen atoms of these compounds. The proton signal of the formyl group at 9.84 ppm, which is present in the spectra of aldehydes **1a–c**, disappears completely in the spectra of hydrazones **2a–c**. The new characteristic signals at 7.80–7.82 ppm due to the protons of N=CH

group appear in the spectra of hydrazones **2a–c**. Compounds **3a–c** show signals at 4.11–4.40 ppm and 4.50–4.72 ppm typical of the oxetanyl group and at 3.87–4.03 ppm, for which the protons of =N−CH_2−C group are responsible. The signals of the CH_3 group in the spectra of compounds **3a–c** are observed at 1.45–1.57 ppm. The signals of =CH_2 group protons of the ethyl vinyl ether moiety in the spectra of compounds **4a,b** are observed at 4.08–4.31 and 4.09–4.28 ppm, respectively. The signals at 6.50–7.86 ppm in the spectra of all the synthesized hydrazones can be assigned to the aromatic protons and to the protons of −CH−N groups.

The mass spectra of new hydrazone compounds show the corresponding molecular ion peaks.

In the synthesis of hydrazones **2a–c**, the strong IR 1650-cm^{-1} absorption band typical of formyl groups disappears. In the synthesis of **3a–c** and **4a,b**, the IR absorption band at around 3300 cm^{-1} which is specific to the absorption of N−H disappears completely. All the final compounds have the characteristic absorption bands of aromatic groups at 3025–3107 cm^{-1} (C−H stretch), at 1568–1599 and 1462–1500 cm^{-1} (C=C stretches), 693–755 cm^{-1} (C−H), and the characteristic absorption bands of aliphatic groups at 2918–2979 and 2868–2880 cm^{-1} (C−H stretches). The IR spectra of compounds **3a–c** and **4a,b** have the characteristic absorption bands of ether groups at 1105–1171 cm^{-1} (C−O−C stretches) and the bands at 1203–1276 cm^{-1} due to the C−N stretching.

The thermal properties of vinyloxyethyl substituted hydrazones were studied by DSC and TGA in the nitrogen atmosphere. The thermal stability of the synthesized compounds is predetermined by the presence of hydrazone moieties [12]. Their 5% weight loss temperatures range from 234 to 279°C, the values of glass transition temperatures T_g and melting points T_m of compounds **3a,b** and **4a,b** are summarized in Table 1.

TABLE 1 Thermal Characteristics of Compounds **3a,b** and **4a,b**

Compound	T_g, [°C]	T^*_m, [°C]
3a	40	80
3b	–3	79
4a	15	79
4b	–	75

*1^{st} heating only.

All the synthesized hydrazones, which were isolated as crystalline materials, can be transformed into the amorphous state. Unfortunately, only **3a** showed T_g well above room temperature. The first DSC heating runs of hydrazones **3a,b** and **4a,b** revealed the melting at 75–80°C. The recooling and second heating run revealed no peaks due to the crystallization and melting, and only the glass-transition temperatures were observed in the DSC heating scans at 40°C for **3a**, −3°C for **3b**, and 15°C for **4a**. The DSC apparatus used did not allow us to fix the glass-transition temperature of **4b.** We can only state that this compound can exist in the solid amorphous state.As an example, the DSC thermograms of compound **3a** are shown in Figure 1.

The DSC results show that 3,4-ethylendioxythiophene-based hydrazone **3a** has higher T_g than the corresponding thiophene-based compound **3b**. The vinyloxyethyl-substituted hydrazone **4a** has lower T_g than the corresponding oxetanyl-substituted hydrazone **3a**.

The newly synthesized hydrazones were also characterized by UV/vis and fluorescence (FL) spectrometry. Terthiophene-based hydrazone **3c** absorbs the electromagnetic radiation in the range 200–500 nm, while 3,4-ethylendioxythiophene- and thiophene-based derivatives absorb in the range 200–400 nm (Fig. 2).

It is evident that the chromophore has a substantial influence on the spectra of the synthesized hydrazones. The low-energy absorption bands of 3,4-ethylenedioxythiophene-based hydrazones **3a**, **4a** show a

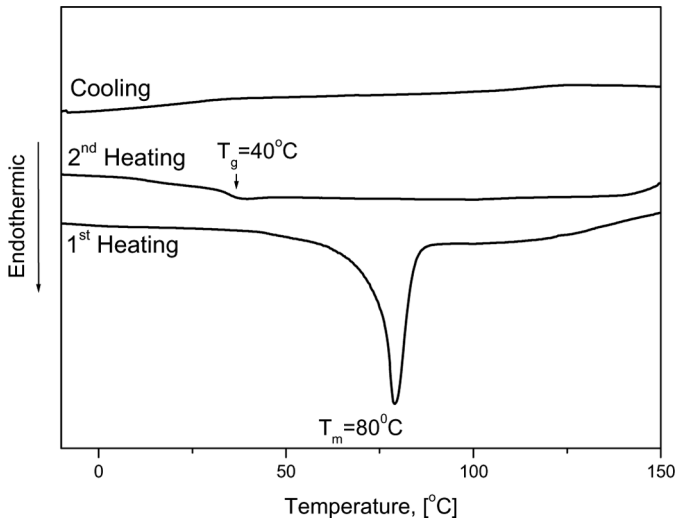


FIGURE 1 DSC curves of compound **3b**. Heating rate 20°C/min.

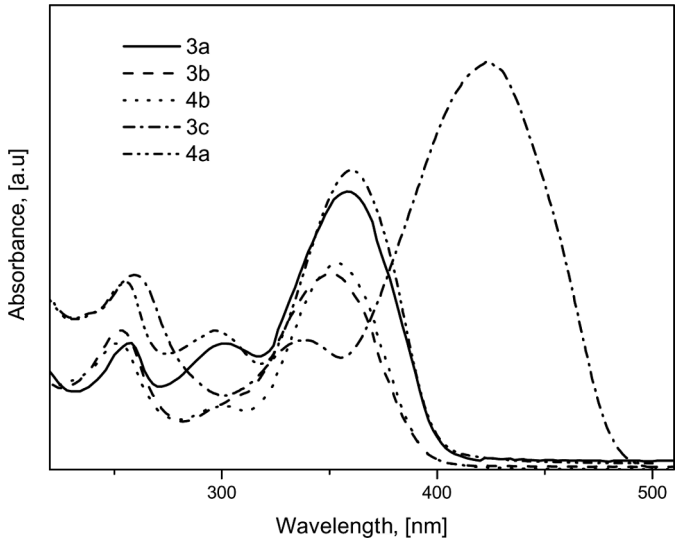


FIGURE 2 UV/vis absorption spectra of dilute THF solutions (10^{-5}) of compounds **3a–c** and **4a,b**.

bathochromic shift of 8 nm with respect of the corresponding absorption bands of thiophene-based hydrazones **3b**, **4b**. The low-energy absorption band of terthiophene-based hydrazone **3c** exhibits a bathochromic shift of 71 nm with respect of the corresponding absorption bands of thiophene-based hydrazones. This observation shows that the effective delocalization of electrons over the hydrazone and terthiopene moieties takes place in a molecule of hydrazone **3c**. The lower ionization potential can be expected for hydrazone **3c** relative to the other newly synthesized hydrazones. The substituent at the nitrogen atom of a hydrazone moiety has small effect on the absorption spectra of hydrazones. The lowest energy absorption band of vinyloxyethyl-substituted hydrazones **4a,b** show a bathochromic shift of ca. 2 nm with respect of the lowest energy absorption band of the corresponding oxetanyl substituted hydrazones **3a–c**. The maxima of the UV absorption and the fluorescence emission spectra of dilute THF solutions of compounds **3a–c** and **4a,b** are summarized in Table 2.

The fluorescence maximum of terthiophene-based hydrazone **3c** is considerably red-shifted as compared with the fluorescence maxima of thiophene- and 3,4-ethylenedioxythiophene-based hydrazones.

An important characteristic of electronically active compounds used in optoelectronic devices is the ionization potential I_p which characterizes the electron releasing work under illumination. The ionization

TABLE 2 UV Absorption and FL Emission (in THF solutions, $c = 10^{-5}$ mol l^{-1}) Maxima of Compounds **3a–c** and **4a,b**

Compound	UV:λ_{max} [nm]	FL[b]:λ_{max} [nm]
3a	359	422
3b	351	421
3c	422	496
4a	361	424, 472[a]
4b	353	415, 450[a]

[a]Shoulder.
[b]For **3a–c** and **4a**, the excitation wavelength was 310 nm, for 4b – 290 nm.

potentials I_p of the hydrazone films **3a–c**, **4a,b** were established from their electron photoemission spectra shown in Figure 3.

The I_p values are summarized in Table 3.

The lowest I_p value of 5.43 eV was observed for compound **3c.** 3,4-Ethylenedioxythiophene-based hydrazones **3a**, **4a** show somewhat higher ionization potentials but lower than that of thiophene-based hydrazones **3b**, **4b.** These observations are consistent with the data of UV/vis spectroscopy. Terthiophene and 3,4-ethylenedioxythiophene-based hydrazones **3a**,**c** and **4a** seem to be suitable for the application

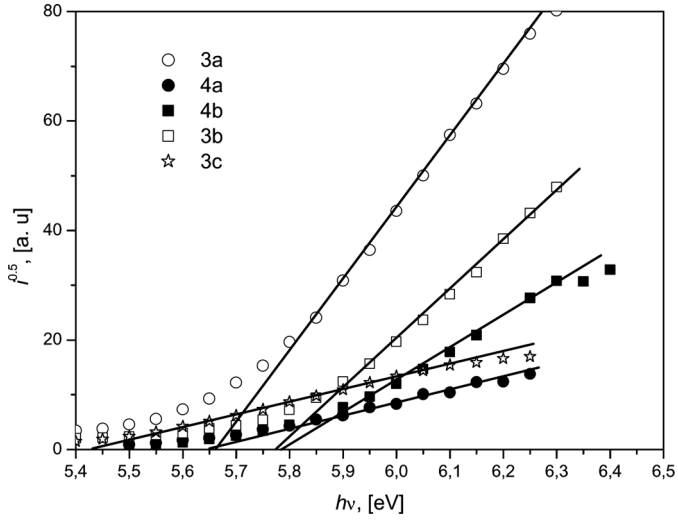


FIGURE 3 Electron photoemission spectra in air of the films of compounds **4a–c, 4a,b**.

TABLE 3 Ionization Potentials of the Films of Hydrazones **3a–c** and **4a,b**

Compound	**3a**	**3b**	**3c**	**4a**	**4b**
I_p, eV	5.66	5.76	5.43	5.60	5.79

as charge-transporting materials for electrophotographic photoreceptors. Holes are easily injected into the charge-transporting layer from a charge-generating layer with I_p close to that of the transport layer. The values of I_p for the conventional charge-generating materials are in the range 5.1–5.6 eV [13].

3,4-Ethylenedioxythiophene- and terthiophene-based hydrazones were subjected to the charge mobility studies by the xerographic time-of-flight technique. Figure 4 shows the electric field dependences for the 50% solid solutions of hydrazones **3c** and **4a** in PC-Z. The linear dependences of the hole drift mobilities on the square root of the electric field intensity are observed.

The room-temperature hole drift mobilities of 50% solid solutions of **3c** and **4a** in bisfenol Z polycarbonate are 2.3×10^{-6} cm^2 V^{-1} s^{-1} and 1.1×10^{-8} cm^2 V^{-1} s^{-1}, respectively, at an electric field intensity of 6.4×10^{-5} V cm^{-1}.

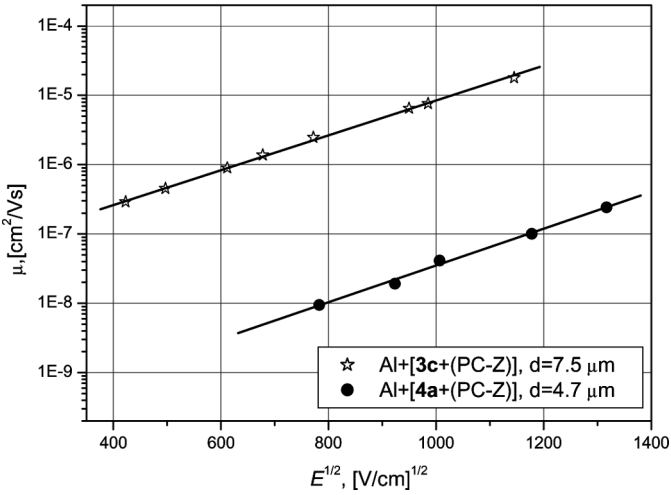


FIGURE 4 Electric field dependences of the hole drift mobilities in the charge-transporting layers of compounds **3c** and **4a** molecularly doped in PC-Z (50% wt.).

CONCLUSIONS

We have synthesized new glass-forming thiophene-based hydrazones containing functional oxetanyl and vinyloxyethyl groups. Their chemical structures were confirmed by ^{1}H NMR, IR spectroscopy, and mass spectrometry. Their optical, thermal, and photoelectrical properties are studied. The hydrazones synthesized can be transformed into the amorphous phase with glass-transition temperatures ranging from -3°C to 40°C. The synthesized compounds exhibit the thermal stability typical of hydrazones. Their 5% weight loss temperatures are in the range from 234 to 279°C. The ionization potentials, measured by the method of electron photoemission in air, are from 5.43 to 5.78 eV. The best hole transport properties were showed by terthiophene-based hydrazone. The time-of-flight experiment showed that the hole drift mobility in molecularly doped bisphenol Z polycarbonate containing 50 wt.% of 2-(5-(thiophen-2-yl)thiophen-2-yl)thiophene-5-carbaldehyde-N-phenyl-N-(3-methyloxetan-3-yl-methyl)hydrazone is 2.3×10^{-6} cm^2 V^{-1} s^{-1} at an electric field intensity of 6.4×10^{-5} V cm^{-1}.

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