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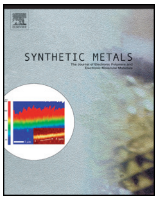

Hole-transporting thiophene-based hydrazones with reactive vinyl groups

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ABSTRACT

Synthesis and optical, thermal, electrochemical, and photoelectrical properties of new thiophene-based hydrazones with reactive vinyl groups are reported. The synthesized compounds were characterized by ^{1}H, ^{13}C NMR, IR, UV/vis, fluorescence, mass spectrometries, and cyclic voltammetry. The synthesized thiophene-based hydrazones form glasses with the glass transition temperatures ranging from 15 °C to 72 °C, as it was elucidated by DSC. Cyclic voltammetry measurements showed that all the synthesized dihydrazones are electrochemically stable up to 0.8 V. Their oxidation potentials are in the range of 0.02–0.55 V. Solid state ionization potentials of these compounds were found to be in the range of 4.82–5.35 eV. Time-of-flight hole-drift mobility in the layer of di-(2-(4-vinylbenzyl)-2-phenyl-1-((thiophene-2-yl)methylene))hydrazone approached 10^{-5} cm^2/V s at high electric field.

1. Introduction

Organic charge-transporting materials are used in optoelectronic and electronic devices such as electrophotographic photoreceptors, organic light-emitting diodes, photovoltaic cells, and field effect transistors [1–6]. To get highly efficient devices, multi-layer structured devices are fabricated with charge injection and transporting layers. However, the preparation of multilayer structures from solution is difficult because the already coated layers can be partially or totally dissolved by the solvent used in the following processing steps. One approach to circumvent this problem is the application of electroactive monomers with photochemically, electrochemically, or thermally polymerisable functional groups [7,8].

Self-polymerization which is also named as the thermal polymerization has several advantages over the other methods. For example, thermal polymerization enables to avoid purification that is rather time consuming for polymers. The charge transporting layers obtained by the self-polymerization of electroactive monomers are free from the residual initiator and the side products which can act as traps for charge carriers. Moreover, thermally cured polymers reveal very good solvent resistance and are electrochemically stable [9–15].

Hydrazones play an important role among organic hole-transporting materials for optoelectronic and electronic devices, especially for electrophotographic photoreceptors, because of their simple synthesis and high charge carrier mobilities [1,16]. It is known that the presence of sulphur or oxygen atoms in the molecules of organic semiconductors improves their characteristics. Therefore thiophene is an interesting constructing unit for the design and synthesis of charge transporting molecules used in organic field effect transistors, organic solar cells, and organic light emitting diodes [17–21]. However, thiophene-based hydrazones until now are poorly studied and represent a relatively small family of organic hole-transporting materials [22–24].

In this study we report on the synthesis and structure–properties relationship of the thermally polymerisable hole-transporting thiophene-based hydrazones with reactive vinyl groups which can be applied in flexible optoelectronic devices.

2. Experimental

2.1. Materials

The starting compounds, i.e., 2-thiophenecarboxaldehyde (**2TA**), 3-thiophenecarboxaldehyde (**3TA**), 2,5-thiophenedicarboxaldehyde (**2TDA**), 3,4-thiophenedicarboxaldehyde (**3TDA**), 2,2′-bithiophene-5-carboxaldehyde (**2BTH**), 2,2′-bithiophene-5,5′-dicarboxaldehyde (**3BTDA**) (all from Aldrich), *N*-phenylhydrazine

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(Fluka), and the required chemicals, i.e., sodium hydride, benzyltrimethylammonium chloride, 4-vinylbenzylchloride (all from Aldrich) were used as received. Organic solvents were purified and dried according to the standard procedures [25].

Di-(2-phenyl-1-((thiophene-2-yl)methylene))hydrazone (**2TDH**), 2-phenyl-1-((thiophene-2-yl)methylene)hydrazone (**2TH**), di-(2-phenyl-1-((thiophene-3-yl)methylene))hydrazone (**3TDH**) were synthesized by the earlier described procedures [23,26,27].

Intermediate compounds **3TH**, **2BTH**, and **2BTDH** were synthesized by condensation of the corresponding aldehyde with phenylhydrazine. The corresponding aldehyde (10 mmol) was dissolved in hot methanol and *N*-phenylhydrazine (20 mmol per one aldehyde group) was added dropwise. After recooling, the crystals were separated by filtration, washed with a large amount of methanol and dried. The products were recrystallized from methanol.

*2-Phenyl-1-((thiophene-3-yl)methylene)hydrazone (**3TH**).* The yield was 89%. MM = 202 g/mol, $C_{11}H_{10}N_2S$. IR (KBr, cm^{-1}): 3315, 3289 (N—H), 3088, 3050, 3002 (Ar. C—H), 1668, 1627 (C═N), 1597 (Ar. C═C), 1570 (N—N), 990, 935, 912 (Alk. C═C). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.5 (s, 1H, N—H), 7.0–7.5 (m, 8H, Ar. and thiophene), 7.5 (s, 1H, $-C\underline{H}=N-$).

*2-Phenyl-1-((5-(thiophen-2-yl)thiophen-2-yl)methylene)hydrazine (**2BTH**).* The yield was 85%. MM = 284 g/mol, $C_{15}H_{12}N_2S_2$. IR (KBr, cm^{-1}): 3314, 3292 (N—H), 3046, 3006 (Ar. C—H), 1667, 1627, 1592 (C═N), 1568, 1546, 1509 (Ar. C═C), 991, 960, 936 (Alk. C═C). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.5 (s, 2H, N—H), 6.8–7.4 (m, 8H, Ar. and thiophene), 7.5 (s, 2H, $-C\underline{H}=N$).

*2-Phenyl-1-((5-(thiophen-2-yl)thiophen-2-yl)methylene)hydrazine (**2BTDH**).* The yield was 86%. MM = 402 g/mol, $C_{22}H_{18}N_4S_2$. IR (KBr, cm^{-1}): 3317, 3293 (N—H), 3066, 3007 (Ar. C—H), 1629 (C═N), 1595 (N—N), 1562, 1511 (Ar. C═C), 1292 (C—N), 986, 935, 910 (Alk. C═C). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.5 (s, 2H, N—H), 6.9–7.4 (m, 14H, Ar. and thiophene), 7.5 (s, 2H, $-C\underline{H}=N-$).

The target compounds **1–6** were synthesized by alkylation [28] of the corresponding hydrazones. The corresponding hydrazone (5 mmol) was dissolved in dry tetrahydrofuran, the catalytic amount of benzyltrimethylammonium chloride and NaH (25 mmol for one formyl group) were added. The mixture was refluxed for 10 min under N_2 atmosphere. Then 4-vinylbenzylchloride (10 mmol for one aldehyde group) was added and the reaction mixture was refluxed for 2 h. After cooling down, the inorganic components were filtered off. The solvent was removed from the filtrate by rotary evaporation. The products were purified by column chromatography using hexane as eluent.

*2-(4-Vinylbenzyl)-2-phenyl-1-((thiophene-2-yl)methylene)hydrazone (**1**).* The yield was 6 g, 75% (dark brown resin). MM = 318 g/mol, $C_{20}H_{18}N_2S$. IR (KBr, cm^{-1}): 3087, 3024, 3007 (Ar. C—H), 2981, 2925, 2856 (Alk. C—H), 1682, 1629 (C═N), 1571 (N—N), 1511 (Ar. C═C), 991, 938, 911 (Alk. C═C), 827, 729, 694 (Alk. C—H). ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.5 (s, 2H, $-C\underline{H_2}$), 5.79 (dd, 1H AMX system of $-CH=\underline{CH_2}$ proton H^X cis J_{AX} = 5.81 Hz), 5.85 (dd, 1H AMX system $-CH=\underline{CH_2}$ proton H^M trans J_{AM} = 5.75 Hz and gem J_{MX} = 5.80 Hz), 6.77 (dd, 1H AMX system $\underline{CH}=CH_2$ proton H^A), 7.0–7.5 (m, 10H, Ar. and thiophene), 7.6 (s, 1H, $-C\underline{H}=N-$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 147.5, 142.4, 137.9, 137.0, 136.9, 136.6, 136.3, 135.1, 129.2, 128.9, 128.6, 127.9, 127.64, 127.2, 126.9, 126.5, 126.4, 126.3, 126.3, 125.9, 125.1, 121.3, 120.9, 118.7, 114.9, 114.8, 114.0, 53.3. Elemental analysis for $C_{20}H_{18}N_2S$ % Calc.: C 75.44, H 5.70, N 8.80, S 10.07; % Found: C 75.49, H 5.65, N 8.75. MS (APCI$^+$, 20 V), m/z = 281, 208.

*Di-(2-(4-vinylbenzyl)-2-phenyl-1-((thiophene-2-yl)methylene))hydrazone (**2**).* The yield was 0.3 g, 45% (dark brown resin). MM = 552 g/mol, $C_{36}H_{32}N_4S$. IR (KBr, cm^{-1}): 3083, 3021, 3005 (Ar. C—H), 2978, 2922, 2840 (Alk. C—H), 1660, 1628, 1596 (C═N), 1567, 1525 (Ar. C═C), 990, 936, 909 (Alk. C═C), 750, 713, 692 (Alk. C—H). ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.6 (s, 4H, $-C\underline{H_2}$), 5.29 (dd, 2H AMX system of $-CH=\underline{CH_2}$ proton H^X cis J_{AX} = 5.25 Hz), 5.79 (dd, 2H AMX system $-CH=\underline{CH_2}$ protons H^M trans J_{AM} = 5.77 Hz and gem J_{MX} = 5.81 Hz), 6.78 (dd, 2H AMX system $\underline{CH}=CH_2$ protons H^A), 6.9–7.5 (m, 20H, Ar. and thiophene), 7.5 (s, 2H, $-C\underline{H}=N-$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 145.8, 141.8, 141.7, 139.7, 137.8, 136.9, 136.9, 136.8, 136.7, 136.2, 135.5, 135.3, 135.0, 133.6, 129.7, 129.0, 128.9, 128.0, 127.8, 127.0, 126.9, 126.02, 125.9, 125.2, 122.6, 122.2, 121.2, 121.0, 120.9, 120.7, 117.4, 115.5, 115.0, 114.9, 114.6, 114.0, 50.9. Elemental analysis for $C_{36}H_{32}N_4S$ % Calc.: C 78.23, H 5.84, N 10.14, S 5.80; % Found: C 78.28, H 5.79, N 10.09. MS (APCI$^+$, 20 V), m/z = 537, 341, 149.

*2-(4-Vinylbenzyl)-2-phenyl-1-((thiophene-3-yl)methylene)hydrazone (**3**).* The yield was 2 g, 65% (yellowish resin). MM = 318 g/mol, $C_{20}H_{18}N_2S$. IR (KBr, cm^{-1}): 3088, 3050, 3002 (Ar. C—H), 1668, 1627 (C═N), 1597 (Ar. C═C), 1570 (N—N), 990, 935, 912 (Alk. C═C), 778, 691 (Alk. C—H). ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.6 (s, 2H, $-C\underline{H_2}$), 5.3 (dd, 1H AMX system of $-CH=\underline{CH_2}$ proton H^X cis J_{AX} = 5.3 Hz), 5.85 (dd, 1H AMX system $-CH=\underline{CH_2}$ proton H^M trans J_{AM} = 5.79 Hz and gem J_{MX} = 5.82 Hz), 6.75 (dd, 1H AMX system $\underline{CH}=CH_2$ proton H^A), 7.0–7.5 (m, 10H, Ar. and thiophene), 7.5 (s, 1H, $-C\underline{H}=N-$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 147.4, 141.6, 141.3, 140.9, 139.9, 138.43, 138.3, 138.0, 137.8, 137.7, 137.7, 137.4, 137.3, 137.3, 137.0, 136.98, 136.8, 130.6, 129.9, 129.0, 128.9, 128.91, 128.83, 128.76, 128.74, 128.59, 128.38, 128.0, 127.9, 127.75, 127.61, 127.49, 127.47, 127.41, 127.15, 127.09, 127.06, 127.0, 126.9, 126.7, 126.0, 125.9, 125.83, 125.51, 125.22, 125.1, 124.6, 124.0, 123.9, 123.94, 123.82, 123.76, 123.74, 123.5, 122.9, 122.66, 122.36, 122.3, 121.4, 121.0, 120.9, 120.1, 119.5, 116.5, 115.8, 115.7, 115.08, 115.0, 114.9, 114.9, 114.8, 114.71, 114.7, 114.5, 114.1, 114.1, 114.0, 50.7. Elemental analysis for $C_{20}H_{18}N_2S$ % Calc.: C 75.44, H 5.70, N 8.80, S 10.07; % Found: C 75.39, H 5.75, N 8.75. MS (APCI$^+$, 20 V), m/z = 208, 117.

*Di-(2-(4-vinylbenzyl)-2-phenyl-1-((thiophene-3-yl)methylene))hydrazone (**4**).* The yield was 2 g, 70% (dark brown resin). MM = 52 g/mol, $C_{36}H_{32}N_4S$. IR (KBr, cm^{-1}): 3061, 3029 (Ar. C—H), 2924 (Alk. C—H), 1711, 1600 (C═N), 1553 (Ar. C═C), 993, 940 (Alk. C═C), 830, 699 (Alk. C—H). ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.7 (s, 4H, $-C\underline{H_2}$), 5.31 (dd, 2H AMX system of $-CH=\underline{CH_2}$ proton H^X cis J_{AX} = 5.29 Hz), 5.62 (dd, 2H AMX system $-CH=\underline{CH_2}$ protons H^M trans J_{AM} = 5.62 Hz and gem J_{MX} = 5.72 Hz), 6.79 (dd, 2H AMX system $\underline{CH}=CH_2$ protons H^A), 6.9–7.7 (m, 20H, Ar. and thiophene), 7.8 (s, 2H, $-C\underline{H}=N-$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 130.3, 130.2, 129.9, 129.5, 128.7, 128.6, 128.5, 128.3, 126.7, 126.5, 46.0. Elemental analysis for $C_{36}H_{32}N_4S$ % Calc.: C 78.23, H 5.84, N 10.14, S 5.80; % Found: C 78.28, H 5.79, N 10.09. MS (APCI$^+$, 20 V), m/z = 503, 355, 208.

*2-(4-Vinylbenzyl)-2-phenyl-1-((5-(thiophene-2-yl)thiophene-2-yl)methylene)hydrazone (**5**).* The yield was 0.5 g, 70% (yellowish crystals). T_m = 109–110 °C. MM = 400 g/mol, $C_{24}H_{20}N_2S_2$. IR (KBr, cm^{-1}): 3046, 3006 (Ar. C—H), 2979 (Alk. C—H), 1667, 1627, 1592 (C═N), 1568, 1546, 1509 (Ar. C═C), 991, 960, 936 (Alk. C═C), 759, 711 (Alk. C—H). ^1H NMR (300 MHz, $CDCl_3$, ppm): 4.6 (s, 2H, $-C\underline{H_2}$), 5.29 (dd, 1H AMX system of $-CH=\underline{CH_2}$ proton H^X cis J_{AX} = 5.28 Hz), 5.8 (dd, 1H AMX system $-CH=\underline{CH_2}$ proton H^M trans J_{AM} = 5.74 Hz and gem J_{MX} = 5.82 Hz), 6.75 (dd, 1H AMX system $\underline{CH}=CH_2$ proton H^A), 6.8–7.4 (m, 14H, Ar. and thiophene), 7.5 (s, 1H, $-C\underline{H}=N-$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 142.8, 141.2, 139.7, 138.5, 138.0, 137.9, 137.7, 137.4, 137.3, 137.1, 136.9, 136.8, 136.7, 136.6, 136.5, 136.4, 136.3, 136.2, 135.2, 134.9, 133.9, 132.5, 132.2, 131.7, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.0, 126.9, 126.9, 125.4, 125.23, 124.0, 123.9, 123.5, 122.0, 121.0, 120.9, 120.8, 119.5, 117.6, 117.2, 116.2, 115.9, 114.9, 114.0, 50.97. Elemental analysis for $C_{24}H_{20}N_2S_2$% Calc.: C 71.96, H 5.03, N 6.99, S 16.01; %