



Hole-transporting phenothiazine-based hydrazones with reactive vinylbenzyl groups



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ABSTRACT

Synthesis and optical, thermal, electrochemical, photoelectrical properties of new phenothiazine-based hydrazones with reactive vinyl groups are reported. The synthesized compounds were characterized by ¹H NMR, IR, UV/VIS, fluorescence, mass spectrometry, and cyclic voltammetry. The oxidation potentials of the phenothiazine-based mono- and dihydrazones are 0.17 V and 0.19 V, respectively. Solid-state ionization potentials of these compounds are 4.97 eV and 4.99 eV, respectively. Hole-drift mobilities in the layer of the phenothiazine-based monohydrazone exceed 10⁻⁵ cm²/Vs at the electric field of 1 × 10⁶ V/cm, at 25 °C. The self-polymerization in the solid state of the synthesized monomers was demonstrated by differential scanning calorimetry.

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1. Introduction

Organic charge-transporting materials are used in optoelectronic devices such as electrophotographic photoreceptors, organic light-emitting diodes, photovoltaic cells, field effect transistors [1–7]. To get highly efficient devices, multilayer structured devices are fabricated. The most challenging task in fabrication of such devices by solution processing is to avoid the interfacial mixing between different layers since most of the organic semiconductors are soluble in common organic solvents. One approach to circumvent this problem is the application of electroactive monomers with photo- or self-polymerizable functional groups [8,9]. The charge-transporting layers obtained by self-polymerization of electroactive monomers are free from the residual initiator which can act as traps for charge carriers. Moreover, thermally cured polymers reveal very good solvent resistance and are electrochemically stable [10–16].

Aromatic hydrazones are known as effective charge-transporting materials for optoelectronic and electronic devices, especially for electrophotographic photoreceptors [1,17]. Since the π-delocalization in the central ring of phenothiazine cation radical was observed [18] the phenothiazine derivatives have attracted considerable research interest due to their simple modification,

strong electron-donating properties, low oxidation potential, and non-planar phenothiazine ring conformation leading to the interesting electrooptical properties, in the last decade [for example, 19,20]. Among the large number of the studies devoted to the phenothiazine-based electroactive compounds only a few publications on the synthesis and properties of the phenothiazine-based hydrazones were reported [21–25]. There is still less research done on the self-polymerization of the aromatic hydrazones. The first possibility of self-polymerization of carbazole- and triphenylamine-based hydrazones with reactive vinyl groups were demonstrated recently [26,27].

In this work we report on the synthesis and properties of phenothiazine-based hydrazones with reactive vinyl groups and demonstrate the possibility of their self-polymerization.

2. Experimental

2.1. Materials

The starting compounds, i.e., 10H-phenothiazine (Aldrich), phenylhydrazine (Fluka), and the required chemicals, i.e., sodium hydride, benzyltrimethylammonium chloride, 4-vinylbenzylchloride, phosphorus(V) oxychloride, potassium hydroxide (all from Aldrich), were used as received. Organic solvents were purified and dried according to the standard procedures [28].

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10-Ethyl-10H-phenothiazinylcarboxaldehyde (**1a**), 10-ethyl-10H-phenothiazinylidicarboxaldehyde (**1b**), 10-ethyl-10H-phenothiazinyl-*N*-phenylhydrazone (**2a**), and 10-ethyl-10H-phenothiazinyl-bis(*N*-phenylhydrazone) (**2b**) were synthesized according to the known procedures [21,25].

Phenothiazine-based hydrazones with reactive vinyl groups **3a** and **3b** (Scheme 1) were synthesized by the general procedure presented below. Compound **2a** or **2b** (1.42 mmol) was dissolved in dry tetrahydrofuran (THF). Then benzyltrimethylammonium chloride (catalytic amount) and NaH (7.1 mmol) were added. This mixture was refluxed for 10 min under N₂ atmosphere before 4-vinylbenzylchloride (7.1 mmol) was added. Then the reaction mixture was refluxed for 2 h. The products were purified by column chromatography using hexane as eluent.

2-(4-Vinylbenzyl)-1-((10-ethyl-10H-phenothiazine-7-yl)methyl)-2-phenylhydrazone (**3a**). The yield was 0.3 g, 60% (yellow crystals). *T*_m = 153 °C. MM = 461 g/mol, C₃₀H₂₇N₃S. IR (KBr, cm⁻¹): 3085 (Ar. C–H), 2982, 2924 (Alk. C–H), 1629 (C=N), 1599 (C=N–N), 1495 (Ar. C=C), 1290 (Ar. C–N), 1258 (Alk. C–N), 990, 908 (C–H of vinyl group). ¹H NMR (300 MHz, CDCl₃, ppm): 0.9 (t, 3H, *J* = 1.7 Hz, –CH₂–CH₃), 3.4 (m, 2H, –CH₂–CH₃), 5.18 (s, 2H, –N–CH₂–), 5.23 (d, 1H AMX system of –CH=CH₂ proton H^X cis *J*_{AX} = 5.26 Hz), 5.75 (d, 1H AMX system –CH=CH₂ proton H^M trans *J*_{AM} = 5.75 Hz and gem *J*_{MX} = 5.80 Hz), 6.7 (dd, 1H AMX system CH=CH₂ proton H^A), 6.95–7.34 (m, 16H, Ar.), 7.64 (s, 1H, –CH=N–). ¹³C NMR (300 MHz, CDCl₃, ppm): 20.1, 35.9, 57.6, 112.9, 113.9, 114.2, 114.8, 119.9, 120.6, 121.3, 122.7, 122.9, 123.7, 124.5, 125.6, 125.8, 127.2, 127.5, 129.4, 132.7, 133.4, 142.7, 144.0. Elemental analysis for C₃₀H₂₇N₃S % Calc.: C 78.06, H 5.90, N 9.10, S 6.95; % Found: C 78.11, H 5.85, N 9.05. MS (APCI⁺, 20V), *m/z* = 242.147, 117.

Di-(2-(4-vinylbenzyl)-1-((10-ethyl-10H-phenothiazine-7-yl)methyl)-2-phenylhydrazone) (**3b**). The yield was 0.75 g, 50% (yellow resin). MM = 695 g/mol, C₄₆H₄₁N₅S. IR (KBr, cm⁻¹): 3083 (Ar. C–H), 2982 (Alk. C–H), 1620 (C=N), 1596 (C=N), 1496 (Ar. C=C), 1332 (Ar. C–N), 1258 (Alk. C–N), 990, 960, 902 (C–H of vinyl group). ¹H NMR (300 MHz, CDCl₃, ppm): 0.9 (m, 3H, *J* = 1.7 Hz, –CH₂–CH₃), 3.4 (m, 2H, –CH₂–CH₃), 5.18 (s, 2H, –N–CH₂–), 5.25 (dd, 1H AMX system of –CH=CH₂ proton H^X cis *J*_{AX} = 5.26 Hz), 5.75 (dd, 1H AMX system –CH=CH₂ proton H^M trans *J*_{AM} = 5.75 Hz and gem *J*_{MX} = 5.80 Hz), 6.7 (dd, 1H AMX system CH=CH₂ proton H^A), 7.15–7.44 (m, 27H, Ar.), 7.64 (s, 2H, –CH=N–). ¹³C NMR (300 MHz, CDCl₃, ppm): 20.0, 35.5, 57.6, 57.7, 112.8, 114.2, 114.7, 120.0, 120.2, 120.6, 121.3, 122.7, 123.0, 123.7, 124.5, 125.6, 125.8, 127.2, 127.5, 129.4, 132.7, 133.4, 142.7, 144.1, 145.5. Elemental analysis for C₄₆H₄₁N₅S % Calc.: C 79.37, H 5.94, N 10.06, S 4.61; % Found: C 79.72, H 5.89, N 10.45. MS (APCI⁺, 20V), *m/z* = 257, 147, 117.

2.2. Instrumentation

¹H NMR and ¹³C spectra were obtained using Varian Unity Inova (300 MHz) spectrometer. The data are given as chemical shifts in δ (ppm), multiplicity, integration downfield from tetramethylsilane. IR spectra were recorded on Perkin Elmer Spectrum BX II FT-IR System. The spectra were performed in KBr pellets or thin layers casted on Si plates. Elemental analyses were performed with an Exeter Analytical CE-440 Elemental Analyzer. Mass spectra were obtained on a Waters ZQ 2000 mass spectrometer (electronic ionization 20 eV). UV spectra of the dilute solutions (10⁻⁴ M) of the synthesized compounds in THF were recorded with Perkin Elmer Lambda 35 spectrophotometer. Fluorescence spectra of the dilute solutions (10⁻⁴ M) in THF were recorded with Hitachi MPF-4 spectrometer at room temperature (excitation wavelength λ_{ex} = 420 nm). Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer DSC 8500 apparatus. The samples were examined at a heating/cooling rate of 10 °C/min under nitrogen

atmosphere. Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA 4000 apparatus under nitrogen atmosphere. The heating rate was 20 °C/min. The melting point of the sample was established using Electrothermal MEL-TEMP. The heating rate was 1 °C/min.

Cyclic voltammetry measurements were performed with a glassy carbon working electrode in a three-electrode cell using Autolab Type III (EcoChemie, Netherlands) potentiostat. The measurements were carried out using solutions (10⁻⁵ M) in dry dichloromethane containing 0.5 M tetrabutylammonium perchlorate at 25 °C, scan rate 50 mV/s. The potentials were measured against Ag/AgNO₃ as reference electrode and the measurements were calibrated with the standard ferrocene/ferrocenium (Fc) redox system [29]. The solid-state ionization potentials (*I*_{pss(CV)}) were calculated using equation *I*_{pss} = *E*_{ox vs. Fc} + 4.8 eV [30], where *E*_{ox vs. Fc} is the oxidation potential of the sample vs. oxidation potential of ferrocene, value for Fc is obtained from the calculated value of –4.6 eV for standard electrode potential (*E*^o) of normal hydrogen electrode (NHE) on the zero vacuum level and the value of 0.2 eV for Fc vs. NHE [31,32]. Electron affinity (EA_(CV)) energy values were calculated using equation: EA_(CV) = *I*_{pss(CV)} – *E*_g^{opt}, where *I*_{pss(CV)} is solid-state ionization potential and *E*_g^{opt} is optical band gap. *E*_g^{opt} was calculated estimating the UV/VIS absorption band edge of a compound λ_{onset} (nm): *E*_g^{opt} = *E*/*e*, where *e* = 1.6 × 10⁻¹⁹ C, *E* = *hc*/λ_{onset}, *h* = 6.63 × 10⁻³⁴ J s, and *c* = 3.0 × 10⁸ m/s.

Charge-transporting properties were estimated by the xerographic time of flight (XTOF) technique [33,34]. The samples for the measurements were prepared by drop casting the solutions of the compounds in THF. The substrate was polyester film with a conductive Al layer. After coating the samples were dried at room temperature for several hours. The thickness of the charge-transporting layer was 1.4 μm for the hydrazone **3a** and 0.8 μm for the hydrazone **3b**. Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with the pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the rate of the surface potential decrease *dU/dt*. The transit time *t_t* for the samples with the transporting material was determined by the kink on the curve of the *dU/dt* transient in double linear scale. The charge drift mobility was calculated by the formula μ ≡ *d*²/*U*₀*t_t*, where *d* is the layer thickness, *U*₀ is the surface potential at the moment of illumination.

3. Results and discussion

3.1. Synthesis

Phenothiazine-based hydrazone monomers with one and two vinyl groups **3a** and **3b** were synthesized by the synthetic route of two steps as shown in Scheme 1. The first step was the condensation of phenothiazine mono- and dialdehydes **1a** and **1b** with *N*-phenylhydrazine to get phenylhydrazones **2a** and **2b**. The second step was alkylation of phenylhydrazones **2a** and **2b** with 1-chloromethyl-4-vinylbenzene using sodium hydride as a catalyst and benzyltrimethylammonium chloride as a phase-transfer agent. The compounds **3a** and **3b** were purified by column chromatography.

The synthesized monomers **3a** and **3b** were found to be soluble in common organic solvents such as acetone, chloroform, THF at room temperature.

Compounds **3a** and **3b** were characterized by ¹H NMR-, IR-, and mass spectrometries. The signals in the ¹H NMR spectra of

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