



Hydrazones containing electron-accepting and electron-donating moieties

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ABSTRACT

Hydrazones containing electron-accepting 1,8-naphthalimide species and electron-donating triphenylamino moieties were synthesized and characterized by nuclear magnetic resonance, infrared spectroscopy, and mass spectrometry. Thermal, optical, electrochemical and photophysical properties of the synthesized derivatives were investigated, their optical and electrochemical band-gap energies and ionization potentials were established. The hydrazones exhibit initial mass loss temperatures in the range of 268–348 °C and can form glasses with glass transition temperatures in the range of 46–142 °C as established by differential scanning calorimetry. Room temperature time-of-flight hole mobilities in the solid solutions of the derivatives in the polymeric host bisphenol-Z polycarbonate (50%) exceeded 10^{-5} cm²/V s at high applied electric fields.

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1. Introduction

Bipolar molecular glasses are of interest for the application in optoelectronic devices such as organic light-emitting diodes. Recently materials showing bipolar charge transport properties have been reported by several groups [1–3]. To achieve a good balance of holes and electrons, both hole and electron-transporting functions should be incorporated into a single bipolar material [4,5]. One promising strategy is to develop bipolar molecules bearing both electron-donating and electron-accepting moieties [6–8]. Such molecules can be also of interest as unimolecular half-subtractors for molecular processors [9].

In this paper, we report the synthesis and a systematic investigation of hydrazones containing both donor (triphenylamino) and acceptor (1,8-naphthalimide) moieties. We have chosen these moieties in the design and synthesis of the bipolar compounds for the following reasons. High electron-affinity of 1,8-naphthalimides determines the possibility of their use as electron-transporting media, and the imide nitrogen makes 1,8-naphthalimides easy to functionalize [10]. Naphthalimide derivatives also represent an attractive class of electron-deficient organic materials for OLED

applications. They exhibit good photochemical stability and high luminescence quantum yields [11]. As a matter of fact, the molecules bearing triphenylamino moiety are widely investigated mainly as hole-transporting materials, and their properties are described in a number of papers and reviews [12–14]. Triphenylamine and its derivatives, with excellent solubility, good stability, and high photoluminescent efficiency, are extensively used in optoelectronic devices [15]. The electron-donating nature of the derivatives of triphenylamine is the basis of their good hole-transporting properties.

2. Experimental Section

2.1. Chemicals

4-Bromo-1,8-naphthalic anhydride, 1-iodoethane (Aldrich), 2-ethylhexylamine (TCl), diphenylamine (Reakhim), 4-Iodoanisole (Aldrich), hydrazine hydrate (Aldrich), and the required chemicals, i.e. magnesium carbonate (Aldrich), potassium hydroxide (Aldrich), were purchased as reagent grade chemicals and used as received. The solvents, i.e. toluene (Aldrich), chloroform (Penta), dimethylformamide (Lachema), dichloromethane (POCH), ethylacetate (Penta), *n*-Hexane (Penta), diethyl ether (Penta), 2-methoxy ethanol (Aldrich), methanol (Penta), were purified and dried using the standard procedures [16].

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2.2. Instrumentation

Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. UV spectra were recorded with Hitachi U-3000 spectrometer. The optical band gap was calculated from absorption edge (λ_{onset}) by conversion of wavelength to the energy using equation: $E_G = hc/\lambda_{\text{onset}}$ [eV] where, h is Planck's constant, c is speed of light in vacuum, λ_{onset} is absorption edge.

Fluorescence (FL) spectra were recorded with an MPF-4 spectrometer. Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectra were obtained using a Varian Unity Inova (300 MHz). All the data are given as chemical shifts in ppm, multiplicity, integration downfield from $(\text{CH}_3)_4\text{Si}$. Mass (MS) spectra were obtained on a Waters ZQ (Waters, Milford, USA). Thermogravimetric analysis was carried out using a Mettler TGA/SDTA851e/LF/1100 apparatus. The measurements were performed under nitrogen flow ($75 \text{ cm}^3 \text{ min}^{-1}$) in a temperature range from -30 to 850 °C at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) was carried out with Q100 TA DSC, with heating/cooling rates of 10 °C/min.

Charge carrier mobility (μ_h) was measured by time-of-flight method [17,18]. The samples for the measurements were prepared by the earlier reported procedure [19]. The electron-transporting layers were cast from the solutions of the compounds synthesized or from solutions of the mixtures of these compounds with polymer host bisphenol-Z polycarbonate (PC-Z) at mass proportion 1:1 in THF. The substrates were polyester film with Al layer. After coating the samples were heated at 80 °C for 1 h. Charge drift mobility was measured in electrophotographic regime. Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with 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 was determined from the kink on the curve of the dU/dt transient in log–log scale. The electron drift mobility was calculated by the formula $\mu_h = d^2/U_0 t_t$, where d is the layer thickness, U_0 – the surface potential at the moment of illumination.

Ionization potentials (I_p) were established by electron photoemission technique in air. The samples were prepared by the earlier reported procedure [20]. They were obtained by casting tetrahydrofuran solutions of the materials on aluminium foil coated with the adhesive layer of methylmetacrylate and metacrylic acid copolymer. The samples before measurements were dried at 80 °C in air for 1 h.

The solutions of the synthesized compounds with the concentration of 1.0 mM were used for cyclic voltamperometry measurements. Electrochemical studies were conducted in 0.1 M solution of Bu_4NBF_4 (Sigma Aldrich 99%) in anhydrous dichloromethane at room temperature.

The electrochemical investigations were carried out using Eco Chemie Company's AUTOLAB potentiostat "PGSTAT20". The results were collected using GPES (General Purpose Electrochemical System) software. The electrochemical cell comprised platinum wire with 1 mm diameter of working area as working electrode, Ag wire – calibrated versus ferrocene/ferrocinium redox couple – as a quasi-reference electrode and platinum coil as auxiliary electrode. Cyclic voltamperometric measurements were conducted at 50 mV/s potential rate.

HOMO and LUMO energies were calculated by the following equations $E_{\text{HOMO}} = -(E_p + 4.8)$ [eV]; $E_{\text{LUMO}} = -(E_n + 4.8)$ [eV] where, E_n and E_p are the onsets of reduction and oxidation potentials versus the Fc/Fc^+ . Electrochemical band gap was obtained from the equation: $E_G = E_{\text{LUMO}} - E_{\text{HOMO}}$ [eV].

2.3. Synthesis

2.3.1. 4-(Di(4-methoxyphenyl)amine)benzaldehyde (**a**) and 4,4'-diformyl-4''-methoxyphenylamine (**b**)

4-(Di(4-methoxyphenyl)amine)benzaldehyde (**a**) and 4,4'-diformyl-4''-methoxyphenylamine (**b**) were synthesized by the method of Vilsmeier [21].

2.3.2. 4-Bromo-N-(2-ethylhexyl)-1,8-naphthalimide (**1**)

Compound **1** was synthesized as described in the literature [22]. A solution of 4-bromo-1,8-naphthalic anhydride (1 g, 3.61 mmol) in 25 ml of dimethylformamide (DMF) was added to a 100 ml three neck round bottom flask equipped with a reflux condenser and a magnetic stirrer. Then 2-ethylhexylamine (0.47 g, 3.61 mmol) was added drop-wise and the reaction mixture was heated up to 110 °C and stirred under nitrogen for 1.5 h. The end of the reaction was detected by TLC (eluent: toluene/ether, 6:1). The reaction mixture was concentrated using rotary evaporator and then the product was precipitated out into 1 N HCl, filtered off and washed with 1 N HCl. The crude product was purified by silica gel column chromatography using acetone and hexane mixture (vol. ratio 1:1.5) as an eluent. Yield: 0.86 g (62%) of yellow crystals. Mp = 82 – 83 °C ^1H NMR spectrum (300 MHz, CDCl_3 , δ , ppm): 8.70 (dd, 1H, $J_{\text{HH}} = 1.13$ Hz, $^4J_{\text{HH}} = 7.31$ Hz, 5- $\text{H}_{\text{Naphthalene}}$), 8.61 (dd, 1H, $J_{\text{HH}} = 1.17$ Hz, $^3J_{\text{HH}} = 8.56$ Hz, 7- $\text{H}_{\text{Naphthalene}}$), 8.45 (d, 1H, $^4J_{\text{HH}} = 7.88$ Hz, 3- $\text{H}_{\text{Naphthalene}}$), 8.08 (d, 1H, $J_{\text{HH}} = 7.87$ Hz, 2- $\text{H}_{\text{Naphthalene}}$), 7.89 (tr, 1H, $J_{\text{HH}} = 7.32$ Hz, $J_{\text{HH}} = 8.52$ Hz, 6- $\text{H}_{\text{Naphthalene}}$), 4.18–4.11 (m, 1H, $-\text{CH}$, 14- $\text{H}_{\text{aliphatic}}$), 1.60–1.34 (m, 10H, $5 \times \text{CH}_2$, 13, 15, 16, 17, 19- $\text{H}_{\text{aliphatic}}$), 0.99–0.90 (m, 6H, $2 \times \text{CH}_3$, 18, 20- $\text{H}_{\text{aliphatic}}$). IR, (in Br), cm^{-1} : 3070 ν (CH_{ar}); 2959, 2926, 2871, 2855 ν ($\text{CH}_{\text{aliphatic}}$); 1702 ν ($\text{C}=\text{O}_{\text{anhydride}}$); 1653, 1590, 1504, 1459 ν ($\text{C}=\text{C}_{\text{ar}}$); 1344, 1231 ν ($\text{C}-\text{N}$); 783 γ (CH_{ar}); 664, 563 ν ($\text{C}-\text{Br}$). ^{13}C NMR spectrum (300 MHz, CDCl_3 , δ , ppm): 164.26, 133.41, 132.32, 131.52, 131.35, 130.89, 130.38, 129.31, 128.34, 123.43, 122.57, 44.54, 38.17, 31.0, 28.95, 24.32, 23.32, 14.34, 10.90. MS (APCI $^+$, 20 V), m/z : 388 ($[\text{M} + \text{H}]^+$). Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{BrNO}_2$: C, 61.86; H, 5.71; Br, 20.58; N, 3.61; O, 8.24. Found: C, 61.79; H, 5.75; Br, 20.62; N, 3.58; O, 8.21.

2.3.3. 4-Hydrazino-N-(2-ethylhexyl)-1,8-naphthalimide (**2**)

4-Bromo-N-(2-ethylhexyl)-1,8-naphthalimide (1.5 g, 3.86 mmol) and hydrazine hydrate (0.38 ml, 7.73 mmol) were dissolved in 40 ml of 2-methoxy ethanol and placed into an oven-dried, 150 ml two-necked round-bottomed flask equipped with a magnetic stir bar under a nitrogen atmosphere. The reaction mixture was refluxed at the room temperature for 1.5 h. The end of the reaction was detected by TLC (eluent: acetone/*n*-hexane, 1:1.5). The reaction mixture was concentrated using rotary evaporator and then the product was precipitated out into 1 N HCl, filtered off and washed with 1 N HCl. The crude product was purified by silica gel column chromatography using acetone and hexane mixture (vol. ratio 1:1.5) as an eluent. Yield: 0.67 g (52%) of yellow crystals. Mp = 81 – 82 °C ^1H NMR spectrum (300 MHz, CDCl_3 , δ , ppm): 8.64 (dd, 1H, $J_{\text{HH}} = 1.01$ Hz, $J_{\text{HH}} = 7.31$ Hz, 5- $\text{H}_{\text{Naphthalene}}$), 8.58 (d, 1H, $J_{\text{HH}} = 8.36$ Hz, 7- $\text{H}_{\text{Naphthalene}}$), 8.09 (d, 1H, $^4J_{\text{HH}} = 1.05$ Hz, 3- $\text{H}_{\text{Naphthalene}}$), 8.06 (d, 1H, $J_{\text{HH}} = 1.06$ Hz, 2- $\text{H}_{\text{Naphthalene}}$), 7.69 (d, 1H, $J_{\text{HH}} = 1.04$ Hz, 6- $\text{H}_{\text{Naphthalene}}$), 6.61 (s, 1H, $-\text{NH}$), 4.15–4.12 (m, 1H, $\text{CH}_{\text{aliphatic}}$), 3.88 (s, 2H, $-\text{NH}_2$), 1.60–1.32 (m, 10H, $5 \times \text{CH}_2$, 13, 15, 16, 17, 19- $\text{H}_{\text{aliphatic}}$), 1.01–0.87 (m, 6H, $2 \times \text{CH}_3$, 18, 20- $\text{H}_{\text{aliphatic}}$). IR, (in Br), cm^{-1} : 3341, 3310 ν (NH_2); 3295 ν (NH); 3073 ν (CH_{ar}); 2950, 2924, 2868 ν ($\text{CH}_{\text{aliphatic}}$); 1693 ν ($\text{C}=\text{O}_{\text{anhydride}}$); 1642, 1616, 1581, 1543 ν ($\text{C}=\text{C}_{\text{ar}}$); 1392, 1358 ν ($\text{C}-\text{N}$); 778 γ (CH_{ar}); ^{13}C NMR spectrum (300 MHz, CDCl_3 , δ , ppm): 133.71, 133.12, 132.71, 132.15, 131.69, 131.30, 131.09, 130.96, 127.16, 125.19, 113.62, 54.13, 53.82, 47.32, 45.03, 32.68, 29.22, 27.91, 27.52. MS (APCI $^+$, 20 V), m/z : 339 ($[\text{M} + \text{H}]^+$). Anal. Calcd. for

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