Dyes and Pigments 113 (2015) 38–46

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Derivatives of indandione and differently substituted triphenylamine with charge-transporting and NLO properties

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ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form
24 July 2014
Accepted 27 July 2014
Available online 7 August 2014

Keywords:
Triphenylamine
Indandione
Glass formation
Nonlinear optical properties
Hole-drift mobility
Ionization potential

ABSTRACT

Derivatives containing electron-donaiting triphenylamino groups and electron-withdrawing indandione moieties were synthesized and their thermal, electrochemical, photoelectrical and nonlinear optical properties were studied. The synthesized compounds form glasses with the glass transition temperatures ranging from 69 to 118 °C. The ionization potentials of the solid samples of the synthesized materials were found to be in the range of 5.48–5.69 eV. Hole-drift mobilities estimated by xerographic time of flight technique in the amorphous layers of 2-({4-[(4-{[(2E)-1,3-dioxo-2,3-dihydro-1H-inden-2-ylidene] methyl}phenyl)(4-methoxyphenyl)amino]phenyl}methylidene)-2,3-dihydro-1H-indene-1,3-dione approached 10^{-4} cm^2/V at an electric field of 6.4×10^5 V cm^{-1}. The nonlinear optical properties of corona poled molecular glasses were characterized by means of Maker fringe technique. Three of investigated compounds exhibited remarkable NLO activities with d_{33} values in the range of 25–100 pm/V.

1. Introduction

Low-molar-mass amorphous molecular materials having intramolecular charge transfer properties represent class of materials which attracts increasing attention of researchers. Such materials are usually functionalized by electron-accepting (A) and electron-donating (D) groups through a π-conjugated bridge which makes it possible to reduce the band gap between ionization potential and electron affinity. Thanks to the presence of delocalized π-electronic systems such compounds have found applications in optoelectronic devices and in dyes sensitized solar cells in particular [1–4]. During the last decade organic compounds having triphenylamine (TPA) moiety have attracted the attention from both experimental and theoretical communities due to their useful photophysical and photoelectrical properties [5]. In particular, these materials have received interest as hole-transporting materials due to their high hole mobilities and easy purification by column chromatography or sublimation techniques [6,7]. TPA derivatives were widely investigated for the use in OFETs [8], photorefractive materials [9], OLEDs [10]. Owing to the noncoplanarity of the three phenyl substituents, TPA derivatives can be viewed as 3D systems. The combination of triphenylamine and linear π-conjugated systems results in amorphous materials with good thermal, electrochemical stability, optical, optoelectronic properties [11–13].

1,3-Indandione is useful starting compound for the synthesis of potentially important compounds. 1,3-Indandione and its derivatives were employed in the synthesis of dyes and pigments [14,15] organic semiconductors [16] and NLO materials [17].

Keeping in mind the above presented information we designed and synthesized derivatives of indandione and differently substituted triphenylamine and studied their thermal, optical, photophysical, electrochemical, photoelectrical and NLO properties.

2. Experimental

2.1. Materials and instrumentation

1,3-Indandione, triphenylamine were purchased from Aldrich, other chemicals were purchased from Chemical Co, Poch, Penta, Lachema, Chempur and used without further purification.

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http://dx.doi.org/10.1016/j.dyepig.2014.07.028
0143-7208/

^{1}H and ^{13}C NMR spectra were recorded using Varrian Unity Inova (300 MHz (^{1}H), 75.4 MHz (^{13}C)) spectrometer at room temperature. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. Mass (MS) spectra were obtained on a Waters ZQ 2000 (Milford, USA). DSC measurements were carried out using a Q100 TA DSC series thermal analyzer at a heating rate of 10 °C/min under nitrogen flow. TGA measurements were performed on a METTLER TOLEDO TGA/SDTA 851^e under nitrogen. Melting points were recorded on Electrothermal MEL-TEMP melting point apparatus. UV absorption spectra were recorded on Perkin Elmer Lambda 35 spectrometer. Fluorescence spectra were recorded with a Perkin Elmer LS 55 and Edinburgh Instruments FLS980 spectrometers. Fluorescence quantum yields (Φ) of the solutions were estimated using integrated sphere method [18]. Integrating sphere (Sphere Optics) coupled to the CCD spectrometer via optical fibre was also employed to measure Φ of the neat films. The cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The working electrode was a glassy carbon, the reference electrode and the counter electrode were Ag/Ag$^+$ 0.01 M and Pt wire, respectively. Argon-purged dichloromethane with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) 0.1 M was used as electrolyte. The experiments were calibrated with the standard ferrocene/ferrocenium redox system [19]. The ionization potentials were measured by the electron photoemission in air method [20]. The samples for the measurements were prepared by dissolving the compounds in THF and by coating on Al plates pre-coated with ca. 0.5 μm thick adhesive layer of the copolymer of methylmethacrylate and methacrylic acid [21]. Xerographic time of flight (XTOF) [22,23] and charge extraction by linearly increasing voltage (CELIV) [24,25] techniques were used to investigate the charge-transporting properties of compounds **1**–**4** using one-electrode (Al/**1**–**4**) and two-electrode (ITO/**1**–**4**/Al) structures. In CELIV dark regime, the initial rise rate provides information on the bulk conductivity of the compounds and the time of extraction current maximum is used for the estimation of the drift mobility of equilibrium charge carriers. For the XTOF measurements the samples based on one-electrode structures were prepared by drop casting of the solutions of the synthesized compounds and of their molecular mixtures with bisphenol-Z polycarbonate (PC-Z) on aluminium coated glass plates. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 1 ns, wavelength 337 nm). The transit time t_t for the samples with the charge-transporting material was determined by the kink on the curve of the dU/dt transient in log–log scale. The charge drift mobility was calculated using the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness, and U_0 the surface potential at the moment of illumination. For the CELIV measurements sandwich-like structures ITO/**1**–**4**/Al with an active area of 7 mm^2 were prepared. The layers were prepared by casting 10 mg/ml chloroform solutions of the compounds onto clean ITO coated glass substrates in a glove box. ITO-coated glass substrates were cleaned by successive washing with acetone, isopropanol, and deionized water in an ultrasonic bath (over 10 min for each operation). The layers of compounds **1**–**4** were 380, 600, 360, and 270 nm thick, respectively. Aluminium electrode was thermally evaporated at 7 Å/s at a pressure of ca. $5\cdot10^{-5}$ mbar. The experimental setup consisted of a delay generator Tektronix AFG 3011 and a digital storage oscilloscope Tektronix DPO 4032.

For the estimation of NLO properties chloroform solutions of compounds **1**–**4** were used to obtain thin spin-coated films on ITO covered glass slides. External electrical field (corona) poling was applied to break symmetry of the chromophores in the molecular glass films. The procedure and custom build corona triode setup was identical to one described in our previous paper [26]. Absorption and reflection spectra of thin films were obtained with Ocean Optics HR4000CG-UV-NIR spectroscopic system. The thickness of the investigated thin films was determined by Dektac 150 profilometer. Refractive indexes of the films were measured by a prism coupler Metricon 2010. In some cases the thickness and the refractive indices were evaluated by a procedure taking advantage of an interference fringe separation in the sample reflection spectrum [27] or Kramers–Kronig equation.

SHG measurements of the corona poled samples were carried out 1–2 days after corona poling to avoid electric field-induced second harmonic generation (EFISHG) contribution caused by the trapped charges. NLO coefficients d_{ij} were obtained by Maker fringe technique (more detailed description of the experiment can be found elsewhere [28]). To calibrate response function of the setup, x-cut quartz crystal ($d_{11} = 0.3$ pm/V) was placed at the same spot and Maker fringe was recorded after investigation of the each sample [29]. The excitation laser was Q-switched DPSS Nd:YVO4 laser NL640 by EKSPLA, pulse energy typically 1–10 μJ, ~10 ns pulse width, repetition rate 40 kHz. The NLO coefficients were obtained by a least square fitting procedure of the theoretical approximation to the experimental curves. The theoretical values of SH intensity were calculated according to Herman–Hayden approach [30], using previously measured refractive indices at 532 nm and 1024 nm, absorption values and thicknesses of the films. The fitting procedure was carried out in two steps: first of all the s–p polarized SHG experimental data were used to calculate d_{31} and then from the p–p data d_{33} was calculated keeping into account that $d_{15} = d_{31}$.

2.2. Synthesis

2.2.1. **4-[(4-Formylphenyl)(4-methoxyphenyl)amino]benzaldehyde (b**, m.p. = 83–84 °C, lit. [31] 80 °C), and **4-[(4-formylphenyl)(4-methylphenyl)amino]benzaldehyde** (**d**, m.p. = 142–143 °C, lit. [32] 145–146 °C), were synthesized the earlier described procedure [33].

2.2.2. **4-[Bis(4-methoxyphenyl)amino]benzaldehyde** (**a**) was synthesized as described in the literature [34]. M.p. = 92–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 9.77 (s, 1H), 7.67–7.62 (m, 2H), 7.18–7.12 (m, 4H), 6.94–6.89 (m, 4H), 6.89–6.84 (m, 2H), 3.84 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ, ppm): 190.37, 157.31, 154.09, 138.81, 131.47, 128.09, 127.74, 116.75, 115.07, 55.52. MS (APCI$^+$, 20 V), m/z: 334 ([M+H]$^+$).

2.2.3. **4-[Bis(4-methylphenyl)amino]benzaldehyde** (**c**) was synthesized as described in the literature [35]. M.p. = 97–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 9.80 (s, 1H), 7.68–7.65 (m, 2H), 7.21–7.7.14 (m, 4H), 7.11–7.08 (m, 4H), 6.98–6.95 (m, 2H), 2.37 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ, ppm): 190.37, 153.70, 143.51, 135.06, 131.33, 130.37, 128.39, 126.42, 118.21, 20.97. MS (APCI$^+$, 20 V), m/z: 302 ([M+H]$^+$).

2.2.4. **2-({4-[Bis(4-methoxyphenyl)amino]phenyl}methylidene)-2,3-dihydro-1H-indene-1,3-dione (1)**. 1,3-Indandione (0.19 g, 1.3 mmol) and 4-[bis(4-methoxyphenyl) amino]benzaldehyde (**a**) (0.4 g 1.43 mmol) were dissolved in 22 mL of butan-1-ol and refluxed for 2 h. Then the mixture was cooled down to the room temperature. The solid precipitate was collected and recrystallized from butan-1-ol to give 0.53 g of red crystals (65% yield). $C_{29}H_{23}NO_4$, MW = 461.51 g/mol, m.p. = 170–171 °C. ^{1}H NMR (300 MHz, DMSO, δ, ppm): 9.90 (s, 1H), 8.55 (t, 3H), 7.96–7.94 (m, 5H), 7.87 (d, J = 8.64 Hz, 1H), 7.77 (d, J = 3.97 Hz, 1H), 7.23 (d, J = 3.75 Hz, 2H), 7.17 (d, J = 8.91 Hz, 1H), 7.11–7.06 (m, 3H), 3.83 (d, J = 3.86 Hz, 6H, 2 × OCH_3). ^{13}C NMR (75.4 MHz, DMSO, δ, ppm): 190.37, 186.25, 154.11, 150.78, 139.56, 134.32, 131.42, 128.86, 127.63, 124.17, 124.12, 121.47, 115.68, 114.88,