



# Twin compounds of phenylethenyl substituted indole as efficient materials for electroluminescent devices



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## ABSTRACT

Twin compounds containing two phenylethenyl substituted indole rings were synthesized by a short multi-step synthetic route. The derivatives were characterized by thermo-gravimetric analysis, differential scanning calorimetry and electron photoemission technique. The materials were found to show very high thermal stability having initial thermal degradation temperatures in the range of 385–390 °C. Glass transition temperatures of the amorphous molecular materials were in the range of 62–95 °C. The electron photoemission spectra of thin layers of the derivatives showed ionization potentials in the range of 5.4–5.5 eV. Hole drift mobilities in thin layers of these derivatives exceed  $6.4 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  at high electric fields at room temperature. These materials have been tested as hole transporting layers in electroluminescent bilayer OLEDs with Alq<sub>3</sub> as the emitter. The device with hole transporting layer comprised of 1,4-di[3-(2-phenylethenyl)indol-1-yl]butane exhibited the best overall performance with low turn-on voltage of 3.4 V, a maximum luminance efficiency of 3 cd/A and maximum brightness of about 1400 cd/m<sup>2</sup>.

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## 1. Introduction

Organic light-emitting diodes (OLEDs) based on organic derivatives attract much attention because of their potential use for lighting applications and in flat panel displays [1–6]. Devices with high efficiency can in general be prepared only by building multi-layer OLEDs [7–9]. One approach that has been widely used to improve efficiency of the devices is the formation of effective hole transporting layers in the multilayer OLEDs.

Carbazole and triarylamine based polymers and low-molecular-weight derivatives are among the most studied materials for electronic applications due to their good electron donating properties and high hole mobility in their layers [10–16]. The derivatives containing electronically isolated triphenylamine or carbazole rings also have high triplet energies and are widely used as host materials for phosphorescent OLEDs [17–23]. We have synthesized earlier series of hole-transporting indole-based derivatives. It was

observed that the new derivatives demonstrate suitable charge injecting and transporting properties for their application in hole transporting layers or for hole transporting host materials [24,25]. In this work, we have designed and synthesized new indole based materials containing two phenylvinyl substituted indole fragments, which were expected to show enhanced hole injection and transport properties and to be suitable as hole transporting materials for multilayer OLEDs. On the other hand the linked indole compounds usually have better amorphous film forming properties and their layers could be formed by cheap solution processing.

## 2. Experimental

### 2.1. Instrumentation

<sup>1</sup>H NMR spectra were obtained using a Varian Unity Inova (300 MHz) apparatus. Mass spectra of the low-molar-mass derivatives were obtained on a Waters ZQ 2000 spectrometer.

Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a TGAQ50 apparatus. The

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TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The electron photoemission method for measurement of ionization potentials ( $I_{EP}$ ) of the solid state layers of the studied compounds was exploited in air [26]. The vacuum deposited layers of the compounds onto commercial indium tin oxide (ITO) coated glass substrates were utilized as the samples for the electron photoemission measurements. The deep-UV deuterium light source ASBN-D130-CM, CM110 1/8 m monochromator, and 6517B Keithley electrometer were used in the experimental setup, which was similar as previously described [27].

The time-of-flight (ToF) method was used to estimate charge-drift mobility of the materials. The charge-drift mobility was calculated by the formula  $\mu = d^2/U \cdot t_{tr}$ , where  $d$  is the layer thickness, and  $U$  the voltage on the electrodes at the moment of illumination of the layers, and  $t_{tr}$  is the transit time, which was taken from the ToF transients. To record the ToF transients for the layer of studied materials, a pulsed third-harmonic Nd:YAG laser EKSPLA NL300 working at a pulse duration of 3–6 ns and the wavelength of 355 nm, a Keithley 6517B electrometer and a digital storage oscilloscope Tektronix TDS 3032C were used in the ToF setup. The ToF samples with following structures of ITO/compound **3** or **4**/Al were prepared. The ITO coated glasses were chemically cleaned using a bath of distilled water and acetone. The organic thin films and layers of aluminium were vacuum-deposited onto the glasses under the vacuum lower than  $5 \cdot 10^{-6}$  mBar.

The electroluminescent devices were fabricated on glass substrates containing a bottom indium tin oxide (ITO) anode (125 nm). Before use for the device fabrication, the ITO-coated substrates were carefully cleaned with acetone and treated with UV/ozone right before deposition of the organic layers. The hole-transporting layers (HTL) of 30 nm thickness were prepared by spin-coating from chloroform solutions (10 mg/ml) of the derivatives **3** or **4**. Tris(quinolin-8-olato)aluminium ( $Alq_3$ ) was used as green light emitter as well as electron transporting layer. Evaporation of  $Alq_3$  (80 nm) and of LiF (1 nm)/Al (100 nm) cathode was accomplished at a pressure of  $4 \times 10^{-4}$  Pa in vacuum evaporation equipment. The final structure of the devices was ITO(125 nm)/HTL(30 nm)/ $Alq_3$ (80 nm)/LiF(1 nm)/Al(100 nm). The luminance of the fabricated OLEDs was measured using a Minolta CS-100 luminance-meter. A Keithley 2400 electrometer was used to measure the current-voltage characteristics of the devices. All the measurements were performed under ambient conditions in air.

## 2.2. Materials

Indole-5-carboxaldehyde (**1**), 1,4-dibromobutane, potassium *tert*-butoxide (*t*-BuOK), KOH, potassium carbonate, diethyl benzylphosphonate and diethyl 4-methylbenzylphosphonate were purchased from Aldrich and used as received.

1,4-Di(3-formylindol-1-yl)butane (**2**) was obtained by reaction 1,4-dibromobutane with an excess of indole-5-carboxaldehyde using similar procedure as described in literature [28].

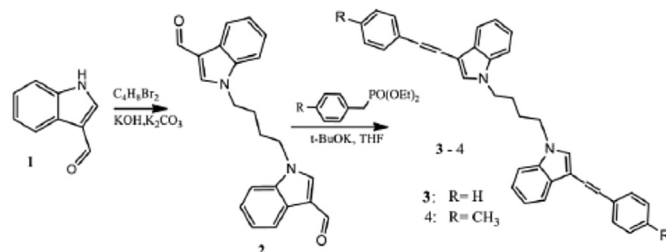
1,4-Di[3-(2-phenylethenyl)indol-1-yl]butane (**3**) was prepared by the reaction of the di-aldehyde **2** with an excess of diethyl benzylphosphonate in dry tetrahydrofuran (THF). Potassium *tert*-butoxide (2.52 g, 26 mmol) and 15 ml of dry THF were placed in a flask at room temperature under nitrogen atmosphere. Diethyl benzylphosphonate (2.26 ml, 11 mmol) were added dropwise to the solution at 0 °C under nitrogen. The reaction mixture was stirred for 20 min. Then 1.5 g (4.4 mmol) of di-aldehyde **2** was added to the reaction mixture. The resulting solution was stirred at room temperature under the basic conditions for 2 h, by which time the starting compound **2** reacted completely. Then the mixture was poured into ice water and extracted with chloroform. Organic

fraction was dried by  $Na_2SO_4$  and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:6) as an eluent. Yield: 0.33 (25%) of white crystals. M.p.: 151 °C (DSC). MS (APCI+, 20 V): 491,2 ( $[M]^+$ , 100%), 492,2 ( $[M+H]^+$ , 75%).  $^1H$  NMR spectrum ( $CDCl_3$ ,  $\delta$ , ppm): 7.98 (d, 2H,  $J = 7.2$  Hz, Ar), 7.49 (d, 4H,  $J = 7.2$  Hz, Ar), 7.36–7.31 (m, 4H, Ar), 7.29–7.25 (m, 4H, Ar), 7.23–7.18 (m, 4H, Ar), 7.13–7.05 (m, 4H,  $2 \times CH=CH$ ), 4.12–3.94 (m, 4H,  $N-CH_2-CH_2-CH_2-CH_2-N$ ), 1.92–1.74 (m, 4H,  $N-CH_2-\oplus CH_2-CH_2-CH_2-N$ ).  $^{13}C$  NMR spectrum ( $CDCl_3$ ,  $\delta$ , ppm): 26.95, 27.35, 43.26, 45.77, 109.28, 109.37, 119.12, 119.41, 120.48, 121.78, 124.23, 126.01, 126.51, 127.28, 128.30, 130.04, 140.21, 140.27. Elemental analysis for  $C_{36}H_{32}N_2$  Calc.: C 87.77, H 6.55, N 5.69; % Found: C 87.81, H 6.58, N 5.64.

1,4-Di[3-[2-(4-methylphenyl)ethenyl]indol-1-yl]butane (**4**) was prepared by the reaction of the di-aldehyde **2** with an excess of diethyl 4-methylbenzylphosphonate. Potassium *tert*-butoxide (2.52 g, 26 mmol) and 20 ml of dry THF were placed in a flask at room temperature under nitrogen atmosphere. Diethyl 4-methylbenzylphosphonate (2.47 ml, 11 mmol) were added dropwise to the solution at 0 °C under nitrogen. The reaction mixture was stirred for 20 min. Then 1.5 g (4.4 mmol) of di-aldehyde **2** was added to the reaction mixture. The resulting solution was stirred at room temperature under the basic conditions for 3 h, by which time the starting compound **2** reacted completely. Then the mixture was poured into ice water and extracted with chloroform. Organic fraction was dried by  $Na_2SO_4$  and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:5) as an eluent. Yield: 0.44 (22%) of white crystals. M.p.: 176 °C (DSC). MS (APCI+, 20 V): 520,3 ( $[M]^+$ , 100%), 521,3 ( $[M+H]^+$ , 46%).  $^1H$  NMR spectrum ( $CDCl_3$ ,  $\delta$ , ppm): 7.97 (d, 2H,  $J = 7.2$  Hz, Ar), 7.38 (d, 4H,  $J = 8.0$  Hz, Ar), 7.27–7.17 (m, 8H, Ar), 7.16–7.01 (m, 8H, Ar and  $2 \times CH=CH$ ), 4.04–3.93 (m, 4H,  $N-CH_2-CH_2-CH_2-CH_2-N$ ), 2.34 (s, 6H,  $2 \times CH_3$ ), 1.87–1.75 (m, 4H,  $N-CH_2-CH_2-CH_2-CH_2-N$ ).  $^{13}C$  NMR spectrum ( $CDCl_3$ ,  $\delta$ , ppm): 21.11, 26.94, 27.40, 45.74, 109.34, 118.81, 119.03, 120.50, 121.46, 121.58, 126.81, 128.29, 129.32, 135.16, 135.32, 135.78, 140.76, 140.88. Elemental analysis for  $C_{38}H_{36}N_2$  Calc.: C 87.65, H 6.97, N 5.38; % Found: C 87.69, H 6.92, N 5.34.

## 3. Results and discussion

The synthesis of twin derivatives (**3** and **4**) containing two phenylethenyl substituted indole rings was carried out by the synthetic route shown below (Scheme 1). Commercially available indole-3-carboxaldehyde (**1**) was firstly used for preparation of the key starting compound- 1,4-di(3-formylindol-1-yl)butane (**2**) by the similar procedure as described in literature [3]. The objective twin derivatives **3** and **4** were then prepared by reaction of the formylindol-1-yl containing dimer **2** with an excess of diethyl benzylphosphonate or diethyl 4-methylbenzylphosphonate, correspondingly. All the synthesized compounds were identified by



Scheme 1. Synthetic scheme of the objective materials **3** and **4**.

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