Synthetic Metals 159 (2009) 492–500

Contents lists available at ScienceDirect

Synthetic Metals

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

Electroluminesent divinylene- and trivinylene-molecules with terminal naphthalimide or phthalimide segments

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ARTICLE INFO

Article history:
Received 28 April 2008
Received in revised form 23 October 2008
Accepted 17 November 2008
Available online 10 January 2009

Keywords:
Heck coupling
Vinylene derivatives
Photophysics
Light-emitting diodes
Electrochemical properties
Electroluminescence

ABSTRACT

Two new linear divinylenes **FN** and **PN** that contained fluorene and phenylene, respectively, as central unit and naphthalimide terminal groups were synthesized by Heck coupling. In addition, two new star-shaped trivinylenes **TPA-P** and **TPP-P** that contained triphenylamine and 2,4,6-triphenylpyridine, respectively, as central core, and terminal phthalimide groups were similarly synthesized. All molecules were very soluble in common organic solvents due to their high fraction of aliphatic moieties which were attached to the central unit and/or the terminal imides. Trivinylenes showed higher thermal stability and higher glass transition temperature (118–126 °C) than divinylenes. **FN**, **PN** and **TPA-P** emitted green-orange light with maximum at 518–586 nm, while **TPP-P** emitted blue light with maximum at 444–462 nm due to the kinked central core of 2,4,6-triphenylpyridine. The maximum luminance among the four molecules is 583 cd/m^2 at current density of 186 mA/cm^2 and applied voltage of 19.5 V based on **TPA-P**, with a luminance efficiency maximum (η_{max}) of 1.7 cd/A.

1. Introduction

Light-emitting polymers, especially p-conjugated polymers with electronically rigid backbones, have received considerable scientific and industrial attention owing to their increasing potential as electronic and optoelectronic devices [1–3].

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have remained the most popular polymers for construction of light-emitting diodes (LEDs). PPVs provide the advantages of high oxidative and thermal stability as well as the ability of tuning the emitted light through chemical modification. The most common methods for this modification are the introduction of electron-donating or -withdrawing substituents [4], the disruption of the conjugation introducing non-conjugated spacers in the main chain [5], and the replacement of phenylene rings by other aromatic rings [6].

Among all the light-emitting polymers so far reported, polyfluorene and its derivatives have emerged as very promising materials because of their unique combination of good thermal stability, high hole mobility, easy processability, and high photoluminescence (PL) quantum yield in the solid state [7–14]. However, the problems encountered with these rod-like polyfluorenes and their derivatives are their tendency to form aggregates [15,16], excimers [17], and/or ketone defects [18,19] in solid state.

Phthalimide and 1,8-naphthalimide compounds are an attractive class of electron-deficient organic materials for fabrication of LEDs with high electron affinities [20]. 1,8-Naphthalimides have wide energy gaps [21–25] and low reduction potentials [26] and therefore can be used as n-type materials in LEDs. On the other hand, the triphenylamine derivative is well-known as a typical hole transporting material and has a hole mobility of 10^{-3} to 10^{-5} cm^2/(V s) [27,28]. Finally, pyridine is a widely used structure for modification of PPV. Poly(*p*-pyridylvinylene) polymers have been extensively investigated and present the advantages of facile n-doping and of tuning their electro-optical properties by coordination of different guests to the lone pair of nitrogen atoms [29–35].

The present investigation describes the synthesis of four new electroluminescent divinylenes and trivinylenes that carry as central unit fluorene, phenylene, triphenylamine or 2,4,6-triphenypyridine and terminal naphthalimide or phthalimide groups. These molecules were successfully prepared by the Heck reaction. Their photophysical, electrochemical and electroluminescent properties were studied and correlated with their chemical structures. Device based on the **TPA-P** shows a maximum η_{max} of 1.7 cd/A and a maximum luminance values of 583 cd/m^2 at current density of 186 mA/cm^2 and applied voltage of 19.5 V. This work resulted in the continuation of our effort for preparing new luminescent molecules that are candidates for various optoelectronic applications [36].

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doi:10.1016/j.synthmet.2008.11.009

2. Experimental

2.1. Characterization methods

IR spectra were recorded on a Perkin Elmer 16PC FT-IR spectrometer with KBr pellets. ^{1}H NMR (400 MHz) spectra were obtained using a Brucker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. The PL spectra were obtained with a Perkin Elmer LS45 luminescence spectrometer. The PL spectra were recorded with the corresponding excitation maximum as the excitation wavelength. TGA was performed on a DuPont 990 thermal analyzer system. Ground samples of about 10 mg each were examined by TGA and the weight loss comparisons were made between comparable specimens.

Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 at a flow rate of 60 cm^3/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 20 °C/min in N_2 with a flow rate of 60 cm^3/min. The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets of 10 mm diameter and ~1 mm thickness prepared by pressing powder of sample for 3 min under 8 kp/cm^2 at ambient temperature. The T_g is assigned by the first inflection point in the TMA curve and it was obtained from the onset temperature of this transition during the second heating. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

To measure the PL quantum yields (Φ_f) degassed solutions of the samples in THF were prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1. The excitation was performed at the corresponding excitation maximum and a solution in 1 M H_2SO_4 of quinine sulfate, which has Φ_f of 0.546 was used as a standard.

Thin films of the samples were prepared from their solutions in THF by spin coating on quartz substrate.

Cyclic voltammetry measurements were carried out in a conventional three-electrode cell using a platinum disk working electrode 2 mm in diameter, a platinum wire as counter electrode, and Ag/AgCl reference electrode on a computer-controlled EG and G Potentiostat/Galvanostat model 283 at room temperature.

OLED were constructed on indium tin oxide (ITO)-coated glass with a sheet resistance of 100 Ω square^{-1}. The ITO-coated glass substrates were etched, patterned, and washed with ethanol, acetone, and $CHCl_3$ sequentially. All device testing were carried out under an ambient atmosphere at room temperature. The EL spectra of the OLED were recorded on a Hitachi F-4500 spectrophotometer. Current–voltage characteristics were measured with a pA meter/DC voltage (DC: direct current) source.

2.2. Reagents and solvents

DMF was dried by distillation over CaH_2. Triethylamine was purified by distillation over KOH. All other reagents and solvents were commercially purchased and were used as supplied.

2.3. Preparation of starting materials

2.3.1. 4-Bromo-N-cyclohexylnaphthalimide (**1**)

Compound **1** was prepared according to a reported method [37] which was modified as follows. 4-Bromo-1,8-naphthalic anhydride (3.00 g, 10.83 mmol) was dissolved by heating in toluene (60 mL). A catalytic amount of triethylamine (~0.5 mL) was added to the solution. Cyclohexylamine (1.29 g, 13.00 mmol) was subsequently added dropwise to the solution. The mixture was refluxed under N_2 overnight. The distilled water was removed using a Dean Stark trap. After cooling, compound **1** precipitated as a pale brown solid. It was recrystallized from ethanol (1.29 g, 33%, mp 198–200 °C).

FT-IR (KBr, cm^{-1}): 3318, 3070, 2924, 2850, 1702, 1662, 1586, 1570, 1448, 1406, 1362, 1344, 1258, 1236, 1188, 1110, 984, 864, 840, 776, 692, 570.

^{1}H NMR 400 MHz ($CDCl_3$, ppm): 8.61–7.54 (m, 5H, aromatic); 4.13 (m, 1H, cyclohexyl proton close to the nitrogen); 1.91–1.92 (m, 10H, other cyclohexyl protons).

2.3.2. 9,9-Dihexyl-2,7-divinylfluorene (**2**)

This compound was prepared by Stille coupling reaction [38] of 2,7-dibromo-9,9-dihexylfluorene with tributylvinyltin in the presence of $PdCl_2(PPh_3)_2$ as catalyst and a few crystals of 2,6-di-*tert*-butylphenol as polymerization inhibitor utilizing toluene as reaction medium. The synthesis and characterization of **2** has been described in our previous publication [39].

2.3.3. 1,4-Bis(dodecyloxy)-2,5-divinylbenzene (**3**)

This compound was similarly prepared by Stille coupling reaction [38] of 1,4-bis(dodecyloxy)-2,5-dibromobenzene according to a reported method [40]. The spectroscopic characterization of **4** conforms to literature [40].

2.3.4. 5-Vinyl-2-cyclohexyl-isoindole-1,3-dione (**4**)

This compound was similarly prepared in 76% yield by Stille coupling reaction [38] of 5-bromo-2-cyclohexyl-isoindole-1,3-dione with tributylvinyltin in the presence of $PdCl_2(PPh_3)_2$ as catalyst and a few crystals of 2,6-di-*tert*-butylphenol as polymerization inhibitor utilizing toluene as reaction medium.

FT-IR (KBr, cm^{-1}): 2926, 2854, 1764, 1706, 1618, 1444, 1370, 1166, 1090, 1018, 920, 752, 704, 636, 540.

^{1}H NMR 400 MHz ($CDCl_3$, ppm): 7.85–7.65 (m, 3H, aromatic); 6.80 (m, 1H, CH_2=*CH*); 5.96 and 5.49 (d of d, J_1 = 17.5 Hz, J_2 = 10.9 Hz, 2H, vinylic); 4.10 (m, 1H, cyclohexyl proton close to the nitrogen), 2.22–1.26 (m, 10H, other cyclohexyl protons).

2.3.5. Tris(4-bromophenyl)amine (**5**)

This compound was prepared by bromination of triphenylamine in chloroform according to a reported method [41].

2.3.6. 2,4,6-Tris(4-bromphenyl)pyridine (**6**)

A mixture of 4-bromobenzaldehyde (1.00 g, 5.40 mmol), 4-bromoacetophenone (2.15 g, 10.80 mmol), CH_3COONH_4 (29.13 g), and glacial acetic acid (15 mL) was refluxed overnight under N_2. After cooling at ~4 °C the precipitate was filtered, washed with acetic acid 50%, then with water, and dried to afford compound **6** (1.42 g, 48%) as a white solid. It was recrystallized from acetone; mp: 265–267 °C.

FT-IR (KBr, cm^{-1}): 1594, 1540, 1486, 1420, 1376, 1178, 1070, 1006, 814.

^{1}H NMR 400 MHz ($CDCl_3$, ppm): 8.03 (d, J = 8.4 Hz, 4H, aromatic); 7.79 (m, 2H, aromatic), 7.66–7.56 (m, 8H, aromatic).

2.4. Preparation of divinylenes

The preparation of **FN** is given as a typical example for the preparation of divinylenes. A flask was charged with a mixture of **1** (0.3712 g, 1.036 mmol), **2** (0.2003 g, 0.518 mmol), $Pd(OAc)_2$ (0.0023 g, 0.010 mmol), P(*o*-tolyl)$_3$ (0.0063 g, 0.021 mmol), DMF (8 mL) and triethylamine (2 mL). The flask was degassed and purged with N_2. The mixture was heated at 90 °C for 12 h under N_2. Then, it was filtered and the filtrate was poured into methanol. The yellow precipitate was filtered and washed with methanol. The crude product was purified by dissolving in THF and precipitating into methanol (0.2548 g, 52%).