Optical Materials 37 (2014) 193–199

Contents lists available at ScienceDirect

Optical Materials

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

Photo- and electroluminescent properties of bithiophene disubstituted 1,3,4-thiadiazoles and their application as active components in organic light emitting diodes

Remigiusz Grykien [a], Beata Luszczynska [a,*], Ireneusz Glowacki [a], Ewa Kurach [b], Renata Rybakiewicz [b], Kamil Kotwica [b], Malgorzata Zagorska [b], Adam Pron [b], Paolo Tassini [c], Maria Grazia Maglione [c], Anna De Girolamo Del Mauro [c], Tommaso Fasolino [c], Romina Rega [c], Giuseppe Pandolfi [c], Carla Minarini [c], Salvatore Aprano [d]

[a] Department of Molecular Physics, Technical University of Lodz, Zeromskiego 116, 90924 Lodz, Poland
[b] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00664 Warsaw, Poland
[c] ENEA C.R. Portici, P.le E. Fermi no. 1, Località Granatello, 80055 Portici, NA, Italy
[d] SESMAT S.r.l., S.S.7 Appia no.36, 82018 San Giorgio del Sannio, BN, Italy

ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 30 April 2014
Accepted 26 May 2014
Available online 20 June 2014

Keywords:
Organic light emitting diodes
Bithiophene disubstituted 1,3,4-thiadiazoles
Host/guest electroluminescent system

ABSTRACT

Photo- and electroluminescence of five bithiophene disubstituted 1,3,4-thiadiazoles, constituting a new class of solution processable materials for organic opto-electronics, were studied. It was found that the introduction of alkyl solubilizing substituents bathochromically shifted the photo- and electroluminescence bands. The most pronounced effect was observed for the substitution at the C_α position which changed the emitting light color from bluish to green. All five derivatives were tested in host/guest type organic light emitting diodes (OLEDs) with either poly(*N*-vinylcarbazole) (PVK) or poly(*N*-vinylcarbazole) + 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PVK + PBD) matrices. The latter matrix turned out especially well suited for these guest molecules yielding devices of varying color coordinates. The best luminance (750 cd/m^2) was measured for 2,5-bis(5′-octyl-2,2′-bithiophene-5-yl)-1,3,4-thiadiazole with the luminous efficiency exceeding 0.4 cd/A.

1. Introduction

Organic opto-electronics started to develop in late 1980s of the past century, after the first report of Tang and Van Slyke on the fabrication of an efficient organic light emitting diode (OLED) [1]. Since that time, the synthesis of new electroluminescent organic molecules and their application as active components in these devices have attracted increasing research interest of chemists [2], physicists [3], materials scientists [4] and electrical engineers [5]. In the past two decades, design and fabrication of OLEDs became a popular field of technological research, as they could serve for flat panel displays or for solid state lighting, exhibiting such advantages as lightness, thinness, high switching speed and wide viewing angle [6]. A part of these researches was dedicated to the development of electroluminescent materials which produce light of the various colors [7–10], including white light emitters (see for example [11]).

Two types of organic light emitting diodes can be distinguished. In the first type, the emitting layer is made of a single semiconductor, in which all phenomena leading to the electroluminescence take place, *i.e.* transport of the charge carriers injected from the electrodes, exciton formation, charge recombination and emission of a quantum of radiation (see for example [2]). Both low [2,11] and high molecular mass [12,13] organic semiconductors can be used as emitters in this type of diodes. In the second type of devices a blend is used [14], in which luminescent “guest” molecules are dispersed in a “host” matrix consisting of one or two semiconductors of a wide energy gap.

In this host/guest configuration the singlet excitons, formed in the host phase as a result of electrical excitation, are transferred to the guest molecule *via* the so called “Förster energy transfer”. Two principal conditions must be fulfilled for this type of energy transfer to occur: (i) the energy levels in the host and in the guest have to be appropriately aligned, in particular the HOMO level of the host must be higher than that of the guest and the LUMO level of the host must be lower than that of the guest; (ii) the emission spectrum of the host must significantly overlap with the guest’s

---

* Corresponding author. Tel.: +48 426313205.
E-mail address: beata.luszczynska@p.lodz.pl (B. Luszczynska).

http://dx.doi.org/10.1016/j.optmat.2014.05.023
0925-3467/

absorption spectrum. In addition, for efficiently performing devices, the content of the guest molecules should be low, in the range of few percent [14]. Since for many host materials the injection of charge carriers directly from the electrode can be difficult, devices using a multilayer configuration are frequently used, in which the active layer is separated from the electrodes by appropriate hole and electron injection/transporting layers (for example [15]).

In this communication, we describe the electroluminescent properties of recently synthesized bithiophene disubstituted 1,3,4-thiadiazole derivatives [16]. We also report on the application of these new electroluminescent materials in host/guest in OLEDs where the host matrix consists of either poly(*N*-vinylcarbazole) (PVK) or PVK blended with 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD).

2. Experimental

Five new compounds were tested as emitting guest molecules in the two types of host matrices (PVK and PVK + PBD), namely: 2,5-bis(2,2′-bithiophene-5-yl)-1,3,4-thiadiazole (abbreviated as **T1**), 2,5-bis(4′-octyl-2,2′-bithiophene-5-yl)-1,3,4-thiadiazole (**T2**), 2,5-bis(3′-octyl-2,2′-bithiophene-5-yl)-1,3,4-thiadiazole (**T3**), 2,5-bis(5′-octyl-2,2′-bithiophene-5-yl)-1,3,4-thiadiazole (**T4**), 2,5-bis(4′,5′-dioctyl-2,2′-bithiophene-5-yl)-1,3,4-thiadiazole (**T5**). Their synthesis is described in detail in the Supporting Information of Ref. [16].

UV–Vis and photoluminescence spectra were recorded on a Carry 5000 (Varian) and on a Fluorog FL3-11 (Jobin–Yvon) spectrometer, equipped with a Xe-lamp as a source of the excitation and a photomultiplier (R-928 model) with the spectral sensitivity range: 200–900 nm for the detector, respectively. The electroluminescence spectra were detected using a specially designed optical system, consisting of custom made optical collector, optical fiber, Micro HR Imaging Spectrograph and a CCD camera (Horiba Jobin–Yvon). The system has flat sensitivity response in the whole wavelength range 350–950 nm.

Two types of OLEDs were fabricated. In diodes of the first type, PVK was used as a sole component of the host matrix in which guest molecules of the **T1** to **T5** series were dispersed. The devices were fabricated on commercial ITO-coated glass substrates (ITO from Delta Technologies Ltd., sheet resistance 10 Ω/□, thickness 200 nm, on Corning Eagle2000™ glass). The ITO electrodes were washed in detergent-containing deionised water at 80 °C using an ultrasound bath, then consecutively rinsed with deionised water and *i*-propanol and finally dried in air at 115 °C for 2 h. In the next step, the ITO electrode was patterned through photolithography and chemical etching (HCl-based solution). Residues of the resist were removed from the surface using oxygen plasma (O_2 = 40 sccm, 0.25 torr, room temperature, 0.21 W/cm^2, 8 min), as recommended in [17]. Commercial PEDOT:PSS (from H.C. Starck) was used as a hole injection layer (HIL). It was spin-coated in air on the patterned ITO electrodes from a water-based solution (5000 rpm for 1 min, 500 rpm/s acceleration), then dried in oven in air at 100 °C for 2 h, yielding a *ca.* 50 nm thick layer. Before drying, the excess of this polymer was removed from outside of the anodes, to avoid any risk of short-circuits with the nearby devices or with the cathode. Blends containing 2 wt% of a given guest compound from the **T1–T5** series were prepared in a chloroform solution and then spin-coated on the top of the PEDOT:PSS layer. The selection of the content of **T1–T5** in the matrix requires a short comment. In principle, the content of the guest molecules in the host matrix should be low since they must be molecularly dispersed in order to assure an effective Förster energy transfer. Phase separation *via* guest molecules agglomeration significantly lowers the effectiveness of this transfer as observed for contents exceeding 2.0%. The next two layers consisted of bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm)) and tris(8-hydroxyquinolinate)aluminum (Alq_3, 10 nm) used as hole blocking and electron transporting materials, respectively. In the last step, Ca/Al, cathode consisting of *ca.* 50 nm thick Ca layer coated with *ca.* 80 nm Al layer was deposited. BCP, Alq_3 and Ca/Al layers were deposited by evaporation in vacuum (10^{-7} mbar) through shadow masks. The deposition rate for all three layers was kept at 1 Å/s. The emitting area of the devices was about 7 mm^2 (cathode diameter 3 mm) (see Fig. 1). The evaporator chamber was directly connected to a glove box, where oxygen and water were both constantly kept at less than 1 ppm. The electro-optical measurements were performed inside this glove box, so no encapsulation was used. The electrical data were acquired using a Keithley 2400 SourceMeter. The optical output was measured using a photodiode (Newport 810UV) faced just in front of each device and connected to a Keithley 6517A electrometer.

In the second type of diodes a (70:30 weight ratio) blend of PVK and PBD was used as a host matrix, instead of pure PVK. The content of the guest compound (again from the **T1**–**T5** series) in the matrix was 2 wt%, as in the previous case. *Ca.* 70 nm thick active layers were spin coated from a chlorobenzene solution (15 mg PVK + PBD dissolved in 1 mL of solvent) on the top of indium tin oxide prepatterned glass substrates (Ossila) and precoated with a *ca.* 20 nm PEDOT:PSS layer. Prior to the deposition of the blend, the PEDOT:PSS layers were annealed at 200 °C for 10 min. To remove the residual amounts of the solvent, the subsequent deposited active layers were

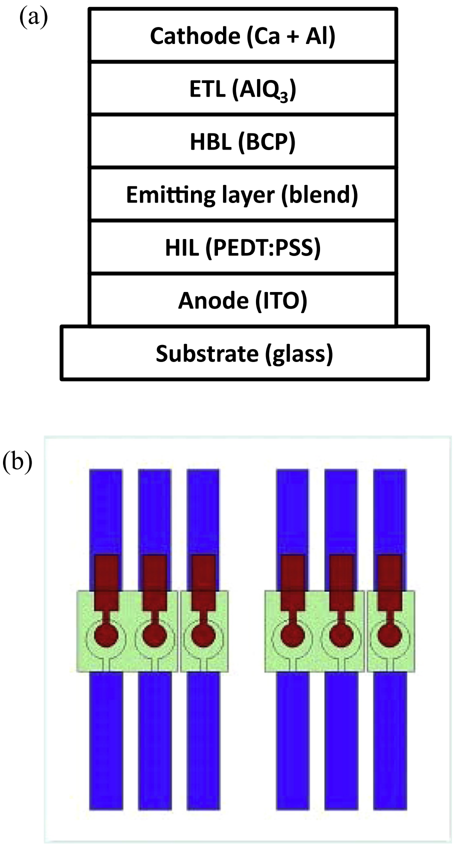

Fig. 1. (a) Schematic cross-sections of the fabricated type 1 OLEDs. (b) Layout of the tested type 1 OLEDs [18]. Colors: blue = anode, green = organic layers, brown = cathode. The emissive area is about 7 mm^2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)