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Energy structure and electro-optical properties of organic layers with carbazole derivative

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ABSTRACT

Phosphorescent organic light emitting diodes are perspective in lighting technologies due to high efficient electroluminescence. Not only phosphorescent dyes but also host materials are important aspect to be considered in the devices where they are a problem for blue light emitting phosphorescent molecules. Carbazole derivative 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1) is a good candidate and has shown excellent results in thermally evaporated films. This paper presents the studies of electrical properties and energy structure in thin films of spin-coated TCz1 and thermally evaporated tris[2-(2,4-difluorophenyl)pyridine]iridium(III) (Ir(Fppy)$_3$). The 0.46 eV difference of electron conduction level between TCz1 and Ir(Fppy)$_3$ compounds was obtained from the cyclic voltammetry and photoconductivity measurements. Temperature modulated space charge limited current (TM-SCLC) method is used to measure the local trapping states for charge carrier in the energy gap. The TM-SCLC measurements for the system TCz1 + 8 wt.% Ir(Fppy)$_3$ show a trapping state with the value of 0.4 eV which is comparable to the conduction level difference of these materials. It allows to conclude that Ir(Fppy)$_3$ molecules act as electron traps in the TCz1 matrix and the TM-SCLC method is applicable to investigate dopants as trapping states. To show the trap effect, an organic light emitting diode was made where the electroluminescent layer was a spin-coated host-guest system of TCz1 with incorporated 8 wt.% Ir(Fppy)$_3$.

1. Introduction

Lighting is one of the organic light emitting diode (OLED) applications where phosphorescent dye is used as an electroluminescent compound. The dye is usually doped at low concentration (less than 10 wt.%) in a conducting matrix. Two conditions should be applied for the matrix. The first condition is bipolar conductivity. Since electroluminescence needs both types of charge carriers, the major importance is given to the materials with bipolar conductivity. In most cases, the mobility of one charge carrier type is at least few orders of magnitude higher than the mobility of the other type. For example, electron mobility in electron-conductive materials such as tris-(8-hydroxyquinolinato)-aluminum is around $3 \cdot 10^{-6}$ cm^2/V·s which is several orders higher than the hole mobility $4 \cdot 10^{-8}$ cm^2/V·s [1]. The same is for the hole-conductive compounds. One of the ways how to deal with it is to synthesize compounds with bipolar conductivity. The second condition is the position of the triplet state energy level of the matrix forming compound with respect to the triplet state energy level of the doped phosphorescent dye molecule. The charge carrier should migrate from the matrix to a dye molecule to generate excited state. Such migration is possible only when the triplet state of the matrix is higher than the triplet state of the dye. Till now many compounds have been synthesized as a matrix for red and green phosphorescence dyes [2–4]. More challenging is a matrix for blue phosphorescent dye where the difference between the first triplet level and the ground state should be around 3 eV. One of the compounds which satisfy both requirements is 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1) (see Fig. 1a). Previously TCz1 was shown as a good host material in thermally evaporated blue emitting OLED structure [5]. The thermal evaporation in vacuum, especially co-deposition, is an expensive method. In this work we show electroluminescence properties of a simple structure device with a spin-coated electroluminescent host–guest system where the guest is blue phosphorescent compound tris [2-(2,4-fluorophenyl)pyridine]iridium(III) (Ir(Fppy)$_3$) (see Fig. 1b) and the host is the previously mentioned bipolar compound TCz1. Cyclometalated iridium (III) complexes are ones of the materials used as dopants in host–guest systems [6–8].

For electroluminescence devices the injection of both electrons and holes is necessary. The aluminum (Al) electrode is applied for electron injection and the indium tin oxide (ITO) electrode — for the hole injection. At first, the values of ionization potential and energy gap of the organic compounds and the work functions of electrodes were compared to build a correct electroluminescence device. The local trapping states

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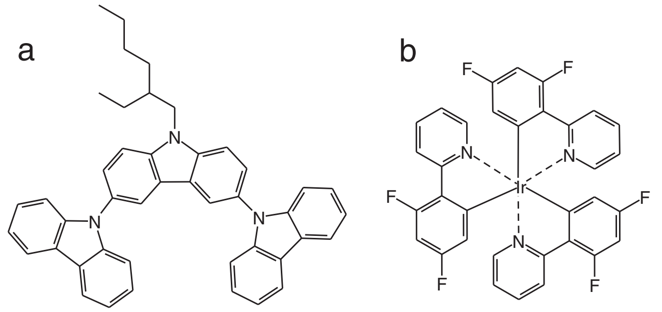

Fig. 1. Chemical structure of (a) the carbazole derivatives TCz1 and (b) the electro phosphorescent compound Ir(Fppy)$_3$.

in pure organic thin films and in a host–guest system were estimated. In this work the results of energy structure (namely, energetical distribution of traps) and the energy gap of thin films of carbazole derivative and carbazole derivative with incorporated Ir(Fppy)$_3$ molecules are compared.

2. Experimental details

2.1. Carbazole derivative

The carbazole oligomer TCz1, whose 9-position is end-capped with an alkyl groups, has been studied (see Fig. 1a). This carbazole oligomer may work as a bipolar charge transport host material for electroluminescence devices [5,9]. The carbazole oligomer TCz1 was synthesized in Kaunas University of Technology.

2.2. Sample preparation

The experiments required two types of samples (see Fig. 2). The first type samples were made for electrical and photoelectrical measurements. They consisted of three layers: ITO/OL/Al (see Fig. 2a) for the electrical measurements and ITO/OL/Au for the photoelectrical measurements, where OL is an organic layer consisting of spin-coated TCz1 or thermally evaporated Ir(Fppy)$_3$, or spin-coated host–guest system of TCz1 with incorporates 8 wt.% phosphorescent iridium complex of Ir(Fppy)$_3$ (TCz1 + 8 wt.% Ir(Fppy)$_3$). Chloroform solution of TCz1 and Ir(Fppy)$_3$ (Sigma Aldrich, catalog number 682594) was admixed to produce a host–guest system. The thickness of obtained organic films was measured with profilometer Dektak 150 and it was between 360 and 390 nm. After spin-coating the samples were dried at 80 °C for 15 min to evacuate the residuals of chloroform. Al or Au electrodes were deposited by thermal evaporation in vacuum so that contact area, i.e. the overlapping area of the cathode and the anode, was 3 mm^2.

The second type samples were made for electroluminescence measurements and the ITO was covered by poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). The samples consisted of ITO/PEDOT:PSS/TCz1 + 8 wt.% Ir(Fppy)$_3$/LiF/Al (see Fig. 2b). Before the deposition of layers, ITO substrates were ultrasonically cleaned for 15 min sequentially in acetone, deionized water and isopropanol, and finally blown dry with nitrogen. PEDOT:PSS (H.C. Starck, Clevious AI 4083) of 40 nm was spin-coated and dried at 160 °C for 10 min. TCz1 + Ir(Fppy)$_3$ with the thickness of 150 nm was spin-coated on top of PEDOT:PSS at 6000 rpm and dried for 15 min at 80 °C. LiF and Al were sequentially deposited by thermal evaporation in vacuum. The thickness of LiF and Al layers was 1 and 100 nm respectively. The active emitting area, i.e. the overlapping area of the cathode and the anode, was 16 mm^2.

2.3. Experimental setups

Current–voltage characteristics were obtained in the regime of space charge limited current (SCLC). The experiment was made in vacuum $8 \cdot 10^{-4}$ Pa at 300 K temperature. Keithley 6487 and Keithley 6514 were used as the voltage source and the electrometer respectively. The temperature modulated space charge limited current method (TM-SCLC) provides for direct measurement of the energy spectrum of charge carrier trapping states. This method was introduced by S. Nešpurek and co-authors [10,11]. TM-SCLC measurements were performed in the temperature range between 250 K and 265 K. Temperature was regulated by the Lakeshore 332 Temperature Controller. The electrical measurements were carried out by the same equipment as the current–voltage measurements.

The photocurrent spectral dependence of ITO/OL/Au devices was measured in the vacuum cryostat system. All measurements were performed in the same vacuum system, using the electrometer Keithley 6517B with an incorporated DC voltage source. Xenon lamp TYP SVX 1450 was used as a light source. Electronically switchable Andover Corporation interference filters (from 360 nm to 700 nm) with the step 20 nm were placed in front of the lamp. The samples were irradiated from the Au electrode side. All measurements were taken for both polarities.

In anthracene-type crystals, the photoconductivity quantum efficiency spectrum $\beta(h\upsilon)$ is determined by the efficiency of thermal dissociated ion pairs which are formed as an intermediate stage of the photogeneration process. It can be described by the Onsager mechanism. The quantum efficiency of photoconductivity $\beta(h\upsilon)$ in the near threshold region can be approximated by

$$\beta(h\upsilon) = A(h\upsilon - E_{th})^n, \tag{1}$$

where n ≈ 5/2 and E_{th} is the threshold energy of conductivity and A is the coefficient [12].

The photoconductivity threshold value is related to the value of adiabatic energy gap E_G^{Ad} [13], i.e.,

$$E_G{}^{Ad} = E_{th} + \Delta E, \tag{2}$$

where ΔE is the effective relaxation energy of the ion pair state.

The Kelvin probe (KP) method was applied to obtain the values of electrode work function [14]. The scanning Kelvin probe equipment SKP5050 was used in the experiments [15]. All work function measurements were performed in ambient conditions and the obtained values were 4.84 ± 0.05, 4.98 ± 0.05 and 4.24 ± 0.05 eV for ITO, Au and Al respectively.

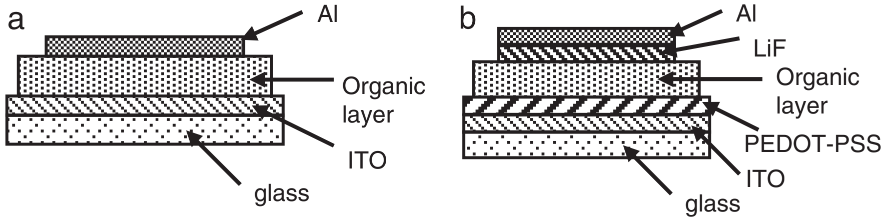

Fig. 2. Scheme of the studied devices.