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Charge transport in 2,6-bis(5′-hexyl-2,2′-bithiophene-5-yl) naphthalene-based organic devices

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ABSTRACT

Organic semiconductor 2,6-bis(5′-hexyl-2,2′-bithiophene-5-yl)naphthalene (H2T26N) is employed as an active layer in organic field-effect transistors (OFETs) or as a hole-transport layer in organic light-emitting diodes (OLEDs). In OFET device the *p*-type conductivity is confirmed and the hole mobility as high as 0.34 $\text{cm}^2/\text{V s}$ is achieved. The emission spectrum of ITO/H2T26N/tris(8-quinolinolato) aluminum (Alq3)/Ca OLED shows emission peaks which cannot be ascribed to either the H2T26N or Alq3 layer. Through studies of photoluminescence spectra and electrochemical properties we demonstrate that the additional feature results from an exciplex at the H2T26N/Alq3 bilayer interface.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention in electronics recently [1,2]. Various fabrication techniques such as the printing method have been envisioned for realizing a low-cost large area display [3]. Basically, the OLED is an injection-type device with two different electrodes that are separated by an organic multilayer. Therefore, the study of charge transport behavior is crucial for understanding as well as device performance improvement. Assuming the energy diagram of the device, many researches have been carried out using low work function electrodes [4] or dipolar layers on the surface of electrodes [5]. Also ideas of utilizing multilayer systems comprising hole- and electron-transport, electroluminescent (emissive) layers, and so forth have been introduced. Multilayer structure of these devices results in steady-state flow of holes and electrons with subsequent recombination inside the emission layer close to the hole transport/emissive layer interface. This device approach is based on light emission from the radiative decay of singlet or triplet excitons in emissive layer. However, the study of the organic–organic interface revealed in certain cases possibility of emission from a charge-transfer excited state complex, also named as exciplex. This intermolecular excited-state complex is identified as an exciplex when one molecule (electron transport layer) is in the excited state and the other (hole transport layer) is in the ground state. In other words, the recombination process is exactly on the material interface where the electron from one material recombines with hole from other material. The exciplex leads to a shift of the emission to lower energies relative to those of the individual components [6], therefore it is usually inefficient. However, it has been reported that by the appropriate selection of materials highly efficient exciplex-based OLED can be achieved [7]. Hence, the materials exhibiting exciplex emission are very important and have high application potential. Exciplex formation at the organic–organic interfaces have recently been reported for several OLED systems [8,9] and extensive studies have been carried out on exciplex emission at different organic heterojunctions, such as m-MTDATA/Alq3 [10], m-MTDATA/Bphen [11], 2-TNATA/Alq3 [12], or TPD/PBD [13]. In addition, exciplex emission provides an alternative mechanism for emission process. It can be used to tune the emitted color [8,14,15] and it is especially interesting for highly efficient blue OLEDs [16,17].

Here we demonstrate application of molecular material we have synthesized, 2,6-bis(5′-hexyl-2,2′-bithiophene-5-yl)naphthalene (H2T26N), as an organic active layer for organic field-effect transistors (OFETs) with *p*-type conductivity and as a hole-transport layer in OLED devices. Furthermore, we report the exciplex formation at the bilayer interface between tris(8-quinolinolato) aluminum (Alq3) layer, which has been widely used as a green-emitting material with electron-transport properties, and H2T26N layer. The analysis results in the reconstruction of the energy band diagram.

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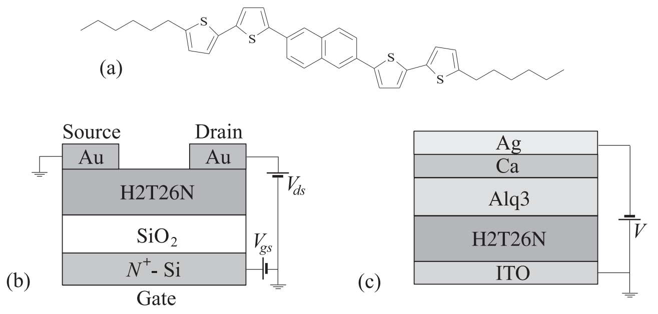

Fig. 1. (a) Schematic view of 2,6-bis(5′-hexyl-2,2′-bithiophene-5-yl)naphthalene (H2T26N) structure. Device structures of H2T26N-based (b) OFET and (c) OLED.

2. Experimental

Tetrahydrofuran (THF) was dried and purified by standard methods before use (Na/benzophenone). 2,6-Dibromonaphthalene, and $PdCl_2(PPh_3)_2$ were purchased from Alfa Aesar. 2-(5′-Hexyl-2,2′-bithiophene-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Sigma Aldrich. Organic semiconductor H2T26N was prepared via microwave assisted palladium catalyzed Suzuki cross-coupling reaction between 2,6-dibromonaphthalene and 2-(5-hexyl-2,2-bithien-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane under inert atmosphere (Ar). Suzuki cross-coupling reaction was performed in Biotage Initiator microwave reactor. Product was several times recrystallized from toluene before use. The detail description of the material synthesis is reported in Ref. [18]. Structure of synthesized organic semiconductor is depicted in Fig. 1(a). Note that synthesis of organic semiconductor H2T26N has been reported already [18,19]. Other organic semiconductors (Alq3 and *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (α-NPD)) used for OLEDs were purchased from Sigma Aldrich.

Silicon wafers with thermally grown oxide (110 nm) with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) surface modification have been used as OFET substrates, see Fig. 1(b). Organic films have been deposited by the vacuum evaporation with a thickness of 40 nm. Selected organic films have been annealed in vacuum better than 5×10^{-6} Pa at the temperature of 150 °C to improve the material crystallinity. Gold electrodes for top-contact OFET were subsequently deposited by thermal evaporation in vacuum through the shadow mask. The channel length/width was 16 μm/2 mm. A double-layer OLED with a structure of ITO/H2T26N (150 nm)/Alq3 (100 nm)/Ca (20 nm)/Ag (100 nm) by the vacuum evaporation as depicted in Fig. 1(c). The working area of OLED was 4 mm^2. As the reference device the typical structure of ITO/α-NPD (150 nm)/Alq3 (100 nm)/Ca (20 nm)/Ag has been employed.

Electrochemical experiments were carried out in a typical three-electrode electrochemical cell equipped with the AC1 sensors (BVT Technologies), which are formed on a corundum ceramic base with applied Pt working electrode (diameter 2 mm), Ag/AgCl reference electrode and Pt auxiliary electrode. Thin H2T26N films were evaporated onto the same type of sensor. According to the IUPAC recommendation [20] the ferrocene couple was used as the reference redox system in this study. Electrochemical analyser, comprising three different modes – cyclic voltammetry, steady-state voltammetry, and voltcoulometry based on the rules published by Thurzo et al., [21], which was recently introduced to the band gap characterization methods [22] was used for the electrochemical determination of HOMO levels. The scan rate of cyclic voltammetry, steady-state voltammetry and voltcoulometry was set to 100, 3, and 3 mV/s, respectively. The duration of the sampling pulse for voltcoulometry was set to 100 ms, the amplitude to −0.05 V. The HOMO response to the applied pulse was sampled at 2 and 10 ms after the trailing edge of sampling pulse. The voltcoulometric signal was evaluated as the difference between thus obtained two values of transient charge. For the electrochemical analysis benzonitrile (for spectroscopy, 99%) was used as a solvent containing 0.1 M supporting electrolyte tetrabutylammonium hexafluorophosphate. Note that H2T26N was dissolved also and the thus the results correspond to the H2T26N solution. For the characterization of evaporated thin film 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile (anhydrous, 99,8%) was used.

Fabricated OFET and OLED devices were characterized by the standard steady-state current-voltage ($I - V$) measurement using Agilent 4155C semiconductor parameter analyser. The optical properties were investigated by the AvaSpec-2048 Fiber Optic Spectrometer (from Avantes company) in transmission setup.

3. Results and discussion

To prove the hole-transport properties of H2T26N the OFET output and transfer characteristics have been investigated. Fig. 2 depicts electrical characteristics of OFET device with organic film annealed in vacuum. The threshold voltage V_{th} and effective mobility μ were estimated by the gradual channel approximation model in the saturation region, see Fig. 2(b),

$$I_{ds} = \frac{WC_g\mu}{2L}(V_{gs} - V_{th})^2, \tag{1}$$

where I_{ds}, V_{ds}, and V_{gs} are drain-source current, drain-source voltage, and gate-source voltage, respectively, as drawn in Fig. 1(b), and C_g is the gate insulator capacitance per unit of area. Estimated mobility and the threshold voltage were 0.34 cm^2/V s and −6 V, respectively, while the OFET devices without the vacuum annealing treatment exhibited mobility and threshold voltage of 0.12 cm^2/V s and −15 V [18], respectively (see Fig. S1 in the Supporting

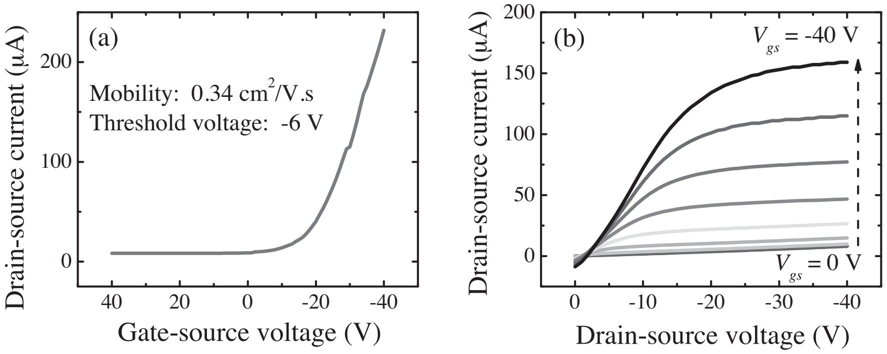

Fig. 2. (a) Transfer characteristics of H2T26N OFET for $V_{ds} = -40$ V. (b) Output characteristics for $V_{gs} = 0\,to - 40$ V with step of 5 V.