Low-voltage organic phototransistors based on naphthyl end-capped oligothiophene nanofibers

CrossMark

Xuhai Liu [a],[*],[1], Luciana Tavares [a], Andreas Osadnik [b], Jens Larsen Lausen [a], Jacob Kongsted [c], Arne Lützen [b], Horst-Günter Rubahn [a], Jakob Kjelstrup-Hansen [a],[*]

[a] NanoSYD, Mads Clausen Institute, University of Southern Denmark, Alsion 2, DK-6400 Sønderborg, Denmark
[b] University of Bonn, Kekulé-Institute of Organic Chemistry and Biochemistry, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany
[c] Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense, Denmark

ARTICLE INFO

ABSTRACT

Organic crystalline semiconductors with highly ordered molecular packing could be vital components in novel low power consumption light sensors due to their unique light absorption and charge carrier transport properties. In this work, we show that nanofibers made from naphthyl end-capped bithiophenes can be used for low-voltage, high responsivity organic phototransistors (OPTs). Density functional theory (DFT) calculations have been carried out to estimate the device properties related to charge transport and photon absorption. In terms of the calculation of the reorganization energy upon charge transfer, we used an extended method to include inter-molecule interactions. Experimentally, the device performance of the 5,5-bis(naphthyl)-2,2′-bithiophene (NaT2) nanofiber OPTs has been compared with that of a thin film OPT with inferior molecular ordering. The better photoresponsivity of the nanofiber OPT compared with the thin film OPT under monochromatic illumination at various wavelengths suggests that the NaT2 nanofiber-based OPTs have great potential to be used as high performance nano-scale light detectors. Moreover, the absorption of the nanofiber-based OPTs is also polarization sensitive, which provides another advantage of nanofiber-based devices in terms of potential novel sensor design.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the past decade an increasing number of investigations has focused on the development of organic field-effect transistors (OFETs) due to their attractive application potential, such as novel, highly efficient light-emitting transistors [1,2], flexible and stretchable organic electronics [3] and organic phototransistors (OPTs) [4,5]. Various advantages of OFETs, incl. low-cost fabrication, large-area processing and mechanical flexibility, make them competitive to the inorganic counterparts [6]. In particular, in addition to the three terminals of a transistor platform, an external light source can be used as the fourth terminal in OPTs to control the density of photo carriers in the transistor channel, thus integrating electrical switching and light detection into an individual optoelectronic device. The possibility of realizing high sensitivity and low noise photoconductive systems render OPTs as an intensive research target, and various active organic semiconductors and metal/dielectric combinations have been investigated [7–11].

The performance of OPTs has been improved significantly. The highest responsivity reported until today

* Corresponding authors. Tel.: +49 351 463 38773 (X. Liu). Tel.: +45 6556 1685 (J. Kjelstrup-Hansen).
 E-mail addresses: xuhai.liu@iapp.de (X. Liu), jkh@mci.sdu.dk (J. Kjelstrup-Hansen).
[1] Present address: Institut für Angewandte Photophysik (IAPP), Technische Universität Dresden, 01069 Dresden, Germany.

observed by Cho et al. was 4300 A W^{-1} under illumination with a light intensity of 7 μW cm^{-2} by using soluble star-shaped oligothiophenes with four-armed π-conjugation paths [12]. However, only few studies in the literature have demonstrated OPTs made of organic crystalline structures [13,14], and particularly, the direct comparison of crystalline materials to amorphous-like thin film-based OPTs is rare [15,16]. Mukherjee et al. obtained 40 times higher photoresponsivity from n-type phototransistors based on solution grown ordered N,N′-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C8) nanowires compared with thin film-based OPTs of the same material [15]. Yu et al. observed that N,N′-bis(2-phenylethyl)-perylene-3,4:9,10-tetracarboxylic diimide (BPE-PTCDI) nanowire-based n-type OPTs exhibit more than 10^3 times larger photoresponsivity than that of thin film OPTs at a gate voltage of 50 V [16]. However, the operating voltage was more than 30 V in both of the aforementioned studies.

In this work, we have fabricated and compared p-type OPTs made of crystalline 5,5-bis(naphthyl)-2,2′-bithiophene (NaT2) nanofibers, and NaT2 thin films with inferior molecular ordering. NaT2 (Fig. 1a) is a recently developed oligothiophene-based molecule, in which the naphthyl end-capping can reduce polymerization resulting in stable optoelectronic device performance [17,18]. In addition, NaT2 can self-assemble into one-dimensional crystalline nanofibers by evaporation under high vacuum conditions onto a muscovite mica surface [19]. As recently demonstrated, a nanofiber roll-transfer technique can be used to easily fabricate bottom gate/bottom contact (BG/BC) organic nanofiber transistors by transferring the nanofibers onto pre-fabricated device substrates [20]. In order to complement our experiments, we also applied density functional theory (DFT) calculations [21] to estimate the performance of the NaT2-based devices. The two governing factors in terms of charge transport, i.e. transfer integral and reorganization energy relevant for hole transfer in NaT2 crystals, have been compared with those of pentacene. In particular, to obtain a more precise value of the reorganization energy, we implemented an extended method to include the inter-molecule interactions, i.e. to use a five-oligomer cluster during the geometry optimization [22].

2. Theoretical details and computational methods

The hopping regime of charge transport in organic materials is important in order to determine the performance of optoelectronic devices. The intersite charge transfer rate k_{ij} in this hopping regime is given in the semi-classical approximation by the Marcus equation [23],

$$k_{ij} = t_{ij}^2 \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_{ij}}} \exp\left(-\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T}\right) \quad (1)$$

where $\hbar$ is the reduced Planck's constant, ΔE_{ij} is the energy difference between the initial and final site energies, k_B and T are the Boltzmann constant and the temperature, respectively. The transfer integral t_{ij} and the reorganization energy λ_{ij} are the predominant factors to determine the

charge transfer rate, whereas ΔE_{ij} is often insignificant [24].

Firstly, the value of the transfer integral t_{ij} depends on the intermolecular overlap of the frontier molecular orbitals of the involved molecules, i.e. the highest occupied molecular orbital (HOMO) for hole transfer and the lowest unoccupied molecular orbital (LUMO) for electron transfer [25]. Since NaT2 is used for p-type transistors in this work, only the transfer integral involving hole transfer is considered. We have implemented a transfer integral calculation method, which involves DFT and considers geometric differences and polarization effects between asymmetric molecules [24,25]. Secondly, the reorganization energy can be determined by summing up two relaxation energies: the relaxation of the donor molecule upon going from the charged-state geometry to the neutral-state geometry λ_0; and the relaxation of the acceptor molecule upon going from the neutral-state geometry to the charged-state geometry λ_1 [25]. We implemented an extended calculation method involving inter-molecule reorganization energy contributions, in which a five-oligomer cluster sliced from the crystal structure is considered [22]. As shown in Fig. 1b, the central oligomer of the cluster is allowed to relax during the geometry optimization, whereas the four peripheral oligomers are fixed in their crystalline positions. This provides a more reasonable manner to estimate the reorganization energy than considering only an individual molecule [22].

The transfer integral calculations were carried out with DFT using the PW91 exchange–correlation functional together with the 6-31G* basis set. It has previously been shown that this combination provides reliable transfer integrals for sulfur-containing materials [26]. The representation for HOMO and LUMO orbitals of NaT2 calculated at the PW91/6-31G* level of theory are shown in Fig. 1c. The reorganization energy calculations were performed at the B3LYP/6-31G** level of theory, since this combination of hybrid functional and basis set yields reorganization energy values closest to experiments [21,25]. All calculations were carried out using the Gaussian 09 package [27].

3. Experimental details

The bottom gate transistor platform consists of a highly n-doped silicon substrate ($\rho = 0.005$ Ω cm) serving as the back gate electrode with a 300 nm thick, thermally grown layer of SiO$_2$ acting as the gate dielectric ($C = 11.5$ nF cm^{-2}). Titanium/gold (2 nm/30 nm) source and drain electrodes were fabricated on the SiO$_2$ layer by optical lithography, electron-beam evaporation and lift-off. The substrates were cleaned by one minute ultrasonic agitation in acetone followed by five minutes rinse in flowing deionized water before organic semiconductor transferring or deposition. NaT2 nanofibers were prepared by vapor deposition of the NaT2 molecules under high vacuum conditions (∼5 × 10^{-7} mbar) onto a freshly cleaved muscovite mica substrate (rate: 0.05 Å s^{-1}, nominal thickness: 25 nm, substrate temperature: 473 K), on which the molecules self-assemble into highly crystalline nanofibers [19]. The NaT2 nanofibers were subsequently transferred onto the