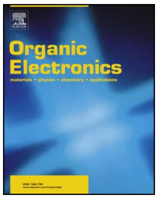
Organic Electronics 54 (2018) 255–260

Contents lists available at ScienceDirect

Organic Electronics

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



High performance p-type chlorinated-benzothiadiazole-based polymer electrolyte gated organic field-effect transistors

Grace Dansoa Tabi[a], Benjamin Nketia-Yawson[a], So-Huei Kang[b], Changduk Yang[b,**], Yong-Young Noh[a,*]

[a] *Department of Energy and Materials Engineering, Dongguk University, 30 Pildong-ro 1-gil, Jung-gu, Seoul 04620, Republic of Korea*
[b] *Department of Energy Engineering, School of Energy and Chemical Engineering, Perovtronics Research Center, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 44919, Republic of Korea*

ARTICLE INFO

Keywords:
Organic field-effect transistors
Conjugated polymers
Benzothiadiazole
Solid-state electrolyte
Threshold voltage shift

ABSTRACT

We report the evaluation of charge transport parameters of four p-type dichlorinated-2,1,3-benzothiadiazole (2ClBT) based conjugated polymers end-capped with different electron-donor units (thiophene (T), thieno[3,2-*b*] thiophene (TT), 2,2′-bithiophene (DT), and (E)-2-(2-(thiophen-2-yl)vinyl)thiophene (TVT)) in electrolyte gated organic field-effect transistors operating at a driving voltage of -2 V. Remarkable hole mobility improvement of 0.13–0.56 $cm^2V^{-1}s^{-1}$ were achieved in 2ClBTs based polymers, with P2ClBT-DT recording the highest mobility of 0.56 $cm^2V^{-1}s^{-1}$ and current on/off ratio $\sim 10^7$. Interestingly, a positive threshold voltage shift (ΔV_{Th}) was observed in the transfer characteristics from the linear to saturation regime of all the 2ClBTs based polymer electrolyte gated OFET devices of $L = 10$ μm, contrary to devices with conventional poly(methyl methacrylate) gate dielectric, which showed a negative ΔV_{Th} shift. Among the 2ClBTs based polymers, P2ClBT-TVT devices showed the lowest mobility and ΔV_{Th} shift, which is attributed to severe ion diffusion in the polymer semiconducting layer owing to the vinyl group backbone susceptible to electrochemical doping. Our results emphasize essential selection consideration of the monomeric moieties, molecular ordering, π-π stacking and backbone planarity of conjugated polymers for electrolyte based organic devices.

1. Introduction

Organic field-effect transistors (OFETs) have gained extensive research interest owing to the high advancement in charge-carrier mobilities and device stability in recent times. The mechanical flexibility, lightweight, low processing temperatures, transparency and cost-effective attributes of OFETs allows straightforward utilization in diverse organic electronic applications [1–6]. Achieving high OFET device performance require critical consideration and optimization of the film morphology and microcrystallinity, molecular orbital energy and π-backbone structure of the organic semiconductor, which are paramount for an efficient charge transport. To this end, various new chemical synthesis and redesign of the polymer semiconductor including the embedding of strong electron-withdrawing groups (such as F, Cl, CN, alkaoyl, fluoroalkyl, etc.) to the conjugated polymer core to tune the molecular orbital energy levels and improve OFET charge-carrier mobilities have been widely reported [7–12]. While several high-performance n-type chlorinated polymer semiconductors have been demonstrated for OFET application [13–17], chlorinated hole-transporting polymers still lag behind those of the n-type counterparts.

Next, to the inherent properties of organic semiconductors, the gate dielectric plays an essential role at the semiconductor/dielectric interface, modulates the density of states by polarization effects and controls voltage operation of OFETs in general. Notably, high capacitance gate dielectric material allows low-voltage driven OFETs [18–21]. Ultrathin film thickness of $\sim$100 nm or less is required for low-voltage OFETs operation using low-*k* polymeric dielectric [19–21]. However, pinhole formation that arises from ultrathin dielectric film layer lower the device yield and reproducibility. Hybrid gate dielectric materials that have been envisioned as an alternative for low-voltage operation include self-assembled monolayers, high-k dielectrics, and solid-state polymer electrolytes [18,22–26].

This study reports improved hole-transport in four dichlorinated-2,1,3-benzothiadiazole (2ClBT) based conjugated polymers containing the various electron-donating co-monomers: (2,5-bis(trimethylstannyl) thiophene (T), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (TT),

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: yang@unist.ac.kr (C. Yang), yynoh@dongguk.edu (Y.-Y. Noh).

https://doi.org/10.1016/j.orgel.2018.01.003
Received 15 October 2017; Received in revised form 2 January 2018; Accepted 2 January 2018

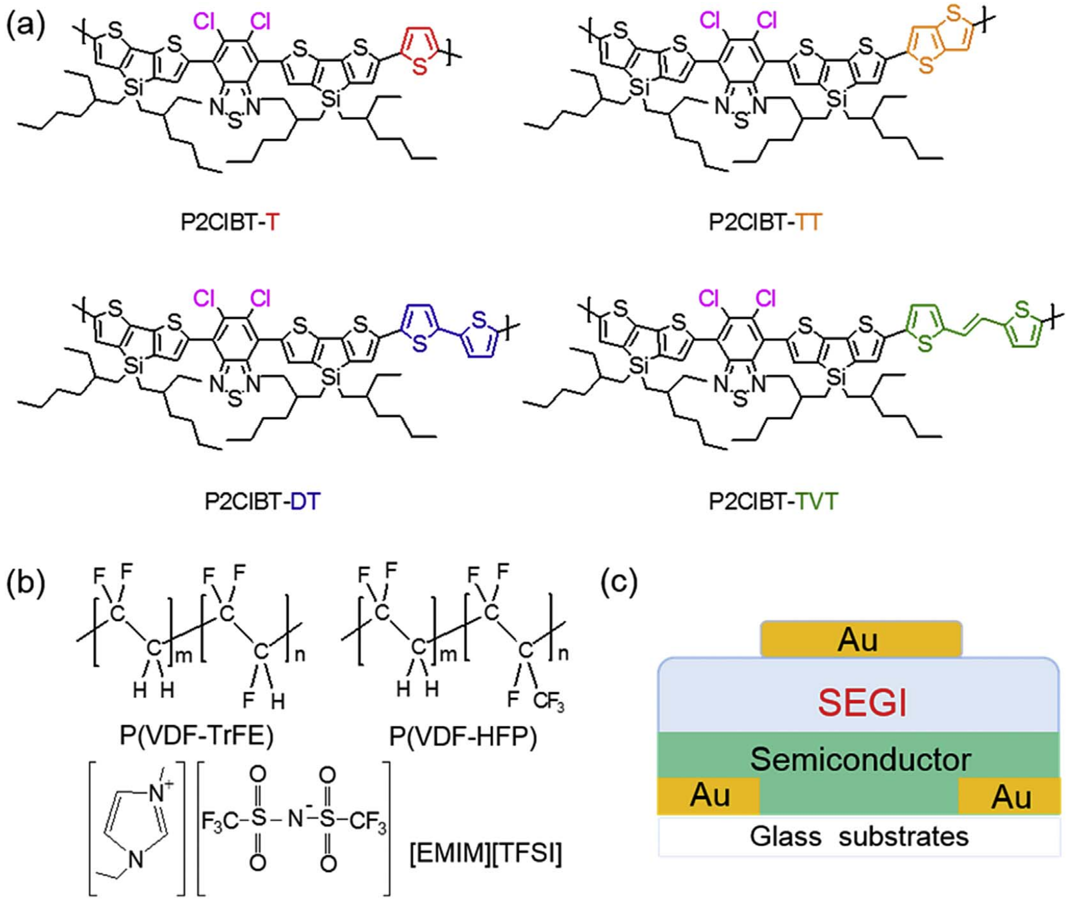


Fig. 1. (a) Molecular structures of 2ClBTs based polymers (b) Chemical structures employed for the formation of the dielectric layer (c) Top gate/bottom contact OFET architecture.

5,5′-bis(trimethylstannyl)-2,2′-bithiophene (DT), and (E)-1,2-bis(5-trimethylstannyl)thiophen-2-yl)ethene (TVT) (Fig. 1(a)) using top gate bottom contacts (TGBC) OFET geometry with solid-state electrolyte gate insulator (SEGI) [12,18]. Our previous publication with these polymers showed lower hole mobilities in the range of 10^{-4}–10^{-1} cm^2/Vs using poly(methyl methacrylate) (PMMA) gate dielectrics. Here, we demonstrate enhanced hole mobility up to about 0.13–0.56 $cm^2V^{-1}s^{-1}$ in 2ClBTs based polymer OFETs at very low driving voltage of -2 V by applying high-capacitance gate dielectric SEGI. The SEGI is composed of high-k polymer poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-HFP)) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([EMIM][TFSI]) (Fig. 1(b)). To the best of our knowledge, this is the first chlorinated polymers to show remarkable hole mobility at the low operational voltage. This paper mainly investigates the relationship between the 2ClBTs based polymer structures and the electrical characteristics of transistors with the SEGI dielectrics.

2. Experimental

2.1. Device fabrication

Top-gate/bottom-contact staggered OFET devices were fabricated on Corning Eagle XG glass substrates. The source and drain electrodes (Au/Ni = 13/3 nm) were patterned using a photolithography process and were deposited onto the glass substrate through thermal evaporation. The channel lengths were 10 and 50 μm and width of 1000 μm. Before the deposition of the active layer, the glass substrates were treated with ozone plasma for 30 min. The 2ClBTs based polymer solutions (5 mg/mL in chlorobenzene (CB)) and poly(3-hexylthiophene-2,5-diyl) (P3HT) polymer solutions (10 mg/mL in CB) were spin-coated at 2000 rpm for 60 s, and then thermally annealed 150 °C for 30 min in a N_2-purged glove box. After, a homogeneous solution of the SEGI formed by a controlled blend of high-k polymer poly(vinylidene fluoridetrifluoroethylene) (P(VDF-TrFE)) (99 vol%) and the ion gel (1 vol%) based on poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDFHFP)) copolymer with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]), ionic liquid, was spin-coated at 2000 rpm for 60 s and baked for 1 h at 80 °C [18]. 40 nm gold (Au) as the gate electrode was thermally evaporated using a metal shadow mask to complete the device fabrication.

2.2. Device characterization

Capacitance measurements from metal-insulator-semiconductor (MIS) structures (area: 200 μm × 200 μm) were performed using HP4284A Precision LCR meter and Keithley 4200-SCS in a N_2-filled glove box. Capacitance-voltage (C-V) measurements were operated at an AC amplitude of 0.2 V and 50–1000 Hz frequency range. OFET devices were tested by Keithley 4200-SCS parameter analyzer in a N_2-filled glove box. The electrical characterization parameters such as threshold voltage (V_{Th}) and field-effect mobility (μ) were calculated from transfer characteristics of devices operated in the linear ($V_D = -1$ V) and saturation ($V_D = -2$ V) regime at a scan rate of 189 mVs^{-1} using the conventional equation: $I_D = (W/2L)\mu C_i(V_G - V_{Th})^2$, where I_D is the drain current, V_G is the gate voltage, W and L are the channel width and length, respectively, and C_i is the dielectric capacitance/unit area. The surface microstructures were examined using non-contact mode atomic force microscopy (Nanoscope, Veeco Instruments, Inc.).