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Complementary-like inverters based on an ambipolar solution-processed molecular bis(naphthalene diimide)-dithienopyrrole derivative

Shree Prakash Tiwari [a], Jungbae Kim [a], Keith A. Knauer [a], Do Kyung Hwang [a], Lauren E. Polander [b], Stephen Barlow [b], Seth R. Marder [b], Bernard Kippelen [a,*]

[a] Center for Organic Photonics and Electronics (COPE), School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
[b] Center for Organic Photonics and Electronics (COPE), School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA

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ABSTRACT

We report on high-mobility top-gate organic field-effect transistors (OFETs) and complementary-like inverters fabricated with a solution-processed molecular bis(naphthalene diimide)-dithienopyrrole derivative as the channel semiconductor and a CYTOP/Al_2O_3 bilayer as the gate dielectric. The OFETs showed ambipolar behavior with average electron and hole mobility values of 1.2 and 0.01 $cm^2\,V^{-1}\,s^{-1}$, respectively. Complementary-like inverters fabricated with two ambipolar OFETs showed hysteresis-free voltage transfer characteristics with negligible variations of switching threshold voltages and yielded very high DC gain values of more than 90 V/V (up to 122 V/V) at a supply voltage of 25 V.

1. Introduction

Organic field-effect transistors (OFETs) are receiving significant attention because of their potential use in low-cost flexible electronic applications such as smart pixels [1], radio-frequency identification tags [2], drivers for electronic paper [3], and driving circuits for flat-panel displays [4]. One approach for enabling these applications is to make use of organic complementary-like logic circuits based on p- and n-channel organic transistors fabricated by vacuum evaporation [5,6]. However, to take advantage of large-area and low-cost processing, solution-processed OFETs are preferred. p-Channel OFETs cast from solution have been reported with saturation mobility values of 2.4 $cm^2\,V^{-1}\,s^{-1}$ by Hamilton et al. [7] and 2.82 $cm^2\,V^{-1}\,s^{-1}$ by Hwang et al. [8]. Recently, p-channel OFETs incorporating a highly crystalline semiconductor with average carrier mobility values of 16.4 $cm^2\,V^{-1}\,s^{-1}$ have been demonstrated with inkjet printing [9]. Solution-processed n-channel OFETs with electron mobility values up to 0.85 $cm^2\,V^{-1}\,s^{-1}$ [10] have also been reported. It is possible to build complementary-like circuits by optimizing a process in which two different semiconductors are inkjet printed and processed on the same substrate: one semiconductor for n-channel and the other for p-channel devices.

Ambipolar OFETs with vacuum-deposited materials have also been demonstrated by bilayers of electron- and hole-transport materials [11–14] or by combining source/drain contact or dielectric engineering with a single pristine semiconductor material [15–17]. However, solution-processed ambipolar OFETs fabricated from a single semiconductor layer with the same metal for both source and drain electrodes, and operating as either p- or n-channel devices depending on the applied voltage, offer the advantage of simplicity.

* Corresponding author. Tel.: +1 404 385 5163; fax: +1 404 385 5170.
E-mail address: kippelen@ece.gatech.edu (B. Kippelen).

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While there are many examples of solution-processed high-performance p- and n-channel OFETs, there are fewer reports on high-performance ambipolar OFETs. Ambipolar properties were first demonstrated in the late 1990s [11,18]; however, research on ambipolar OFETs intensified from around 2003 [19–21]. In the same period, complementary-like circuits composed of ambipolar OFETs were demonstrated using either single-component solution-processed organic semiconductors or a blend of electron- and hole-transport materials [22–26]. Meijer et al. demonstrated solution-processed ambipolar OFETs and complementary-like circuits with a blend of electron- and hole-transport materials and with single-component ambipolar material showing very low electron and hole mobility values on the order of 10^{-5} $cm^2\,V^{-1}\,s^{-1}$ [22]. Later, Anthopoulos et al. reported organic complementary-like inverters employing methanofullerene-based ambipolar field-effect transistors with an electron mobility of 0.01 $cm^2\,V^{-1}\,s^{-1}$ and a hole mobility of 0.008 $cm^2\,V^{-1}\,s^{-1}$ [23]. Kim et al. have demonstrated ambipolar transistors and complementary-like inverters using a bottom-gate, bottom-contact structure on silicon with gold source/drain electrodes and a new donor–acceptor copolymer semiconductor [24]. These transistors exhibited mobility values of up to 0.04 $cm^2\,V^{-1}\,s^{-1}$ for electrons and 0.003 $cm^2\,V^{-1}\,s^{-1}$ for holes in the saturation regime and inverters achieved a static (DC) gain value of 30 V/V. Roelofs et al. have reported ambipolar OFETs with a bottom-gate and gold bottom-contacts and a semiconductor of poly(diketopyrrolopyrrole-terthiophene). The OFETs had electron and hole mobility values of 0.02 $cm^2\,V^{-1}\,s^{-1}$ and complementary-like inverters had a gain of 20 V/V [27]. Recently, we reported that solution-processed films of a molecule in which two naphthalene diimide (NDI) units are bridged by a dithienopyrrole (DTP), 2,2′-(4-*n*-hexyl-4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole-2,6-diyl)bis(*N*,*N*′-bis(*n*-hexyl)naphthalene-1,4:5,8-bis(dicarboximide) (NDI_2-DTP, Fig. 1), exhibits hole and electron mobility values of up to 0.0098 and 1.5 $cm^2\,V^{-1}\,s^{-1}$, respectively, in a top-gate bottom-contact field-effect transistor geometry [28].

Here, we demonstrate top-gate OFETs and inverters fabricated using solution-processed NDI_2-DTP and a CYTOP/Al_2O_3 bilayer as a channel semiconductor and a gate dielectric material, respectively. The use of the top-gate device geometry with the bilayer gate dielectric allows comparatively low voltage operation with remarkable long-term environmental and operational stability [29]. Complementary-like inverters composed of these ambipolar OFETs showed hysteresis-free voltage transfer characteristics and yielded very high DC gain values of more than 90 V/V (up to 122 V/V).

2. Fabrication and electrical characterization

Top-gate OFETs were fabricated to study the ambipolar performance of NDI_2-DTP. The chemical structure of NDI_2-DTP is shown in Fig. 1a. Here, a CYTOP/Al_2O_3 bilayer was used as a gate dielectric material. Fig. 1b shows the structure of the devices. Gold (50 nm) source and drain electrodes were deposited by thermal evaporation through a

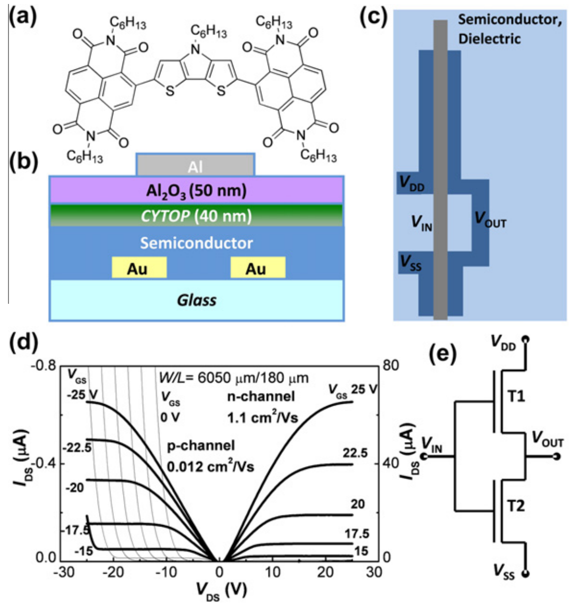

Fig. 1. (a) Chemical structure of NDI_2-DTP, (b) device structure of a top-gate OFET, (c) structure of a complementary-like inverter with two ambipolar OFETs, (d) output characteristics of a representative OFET with NDI_2-DTP exhibiting an electron mobility of 1.1 $cm^2\,V^{-1}\,s^{-1}$ and a hole mobility of 0.01 $cm^2\,V^{-1}\,s^{-1}$ in the saturation regime, and (e) schematic of a complementary-like inverter, with T1 acting as a p-channel device and T2 as an n-channel device.

shadow mask onto Corning glass substrates (roughness < 2 nm). Thin films of NDI_2-DTP [28] were deposited by spin-coating a 30 mg/mL solution in dichlorobenzene. The thin films were then annealed at 100 °C for 15 min. CYTOP solution (CTL-809 M, 9 wt.%) was diluted with solvent (CT-solv.180) to make a 2 wt.% solution which was spin-coated at 3000 rpm for 60 s to form a 40 nm-thick CYTOP layer. The CYTOP film was annealed at 100 °C for 20 min. Al_2O_3 (50 nm) films were then deposited by atomic layer deposition at 110 °C using a Savannah 100 system from Cambridge Nanotech. Finally, Al (150 nm) gate electrodes were deposited by thermal evaporation through a shadow mask. All current–voltage ($I-V$) characteristics were measured in a N_2-filled glove box (O_2, H_2O < 0.1 ppm).

The output (I_{DS} vs. V_{DS}) and transfer (I_{DS} vs. V_{GS}) characteristics were measured using an Agilent E5272A source/monitor unit. The mobility (μ) and threshold voltage (V_{TH}) values were extracted from the highest slope of $|I_{DS}|^{1/2}$ vs. V_{GS} plots in the saturation regime of the transfer characteristics. Average values of mobility and threshold voltage were extracted from 4 to 6 devices fabricated with two different channel widths (W) of 2550 and 6050 μm and the same channel length (L) of 180 μm from a single substrate. The capacitance density of the gate dielectric was measured from parallel plate capacitors fabricated using the same procedures as described above on independent substrates with a geometry of glass/Au/CYTOP (40 nm)/Al_2O_3 (50 nm)/Al (measured at a frequency of 1 kHz) and areas ranging from 1 mm^2 to 4 mm^2. A capacitance density of 34.5(±0.1) nF cm^{-2} was obtained from 4 different batches of samples.

Complementary-like inverter circuits were fabricated using two ambipolar transistors with a channel length of 180 µm and different channel widths of 6050 and 2550 µm, respectively, as shown in Fig. 1c. A common gate electrode, which works as the input (V_{IN}) of the inverter circuit, was thermally deposited for both OFETs through a shadow mask. Since the mobility for p-channel operation for OFETs with NDI_2-DTP is lower than for n-channel operation, the transistor with larger width (6050 µm) was chosen for p-channel operation.

3. Device and inverter results

The output characteristics of a representative OFET with NDI_2-DTP are shown in Fig. 1d. This device exhibits electron and hole mobility values of 1.1 and 0.012 $cm^2 V^{-1} s^{-1}$ and a V_{TH} of +13.7 and −13.0 V during n- and p-channel operation, respectively.

Device batches 1 and 2 were fabricated using NDI_2-DTP from the same synthetic batch, whereas device batch 3 used NDI_2-DTP prepared and purified independently. Table 1 summarizes the results obtained from the various batches. As shown in Table 1, batch-to-batch variations in the electrical properties of the devices are observed, showing average electron-mobility values varying from 0.8(±0.2) to 1.2(±0.3) $cm^2 V^{-1} s^{-1}$ and average hole-mobility values varying from 0.007(±0.003) to 0.009(±0.004) $cm^2 V^{-1} s^{-1}$.

Fig. 1e shows the schematic of a complementary-like inverter realized with two ambipolar OFETs, T1 and T2. In complementary-like operation, T1 (W = 6050 µm) acts as the p-channel device and T2 (W = 2550 µm) acts as the n-channel device. Here, V_{IN} is varied from 0 to 25 V, and V_{DD} and V_{SS} are fixed at 25 and 0 V, respectively. The output characteristics of both T1 and T2 are shown in Fig. 2a and b. A hole mobility value of 0.007 $cm^2 V^{-1} s^{-1}$ with a threshold voltage value of −12.6 V and an electron mobility value of 0.86 $cm^2 V^{-1} s^{-1}$ with a threshold voltage value of 13.5 V were obtained from T1 and T2, respectively. The static performance of an inverter is evaluated by the DC gain values obtained from the measured voltage transfer characteristics. The operation of a complementary inverter can be explained by two series-connected, voltage-dependent variable resistors. In general, for a given supply voltage, V_{DD}, the switching voltage (V_M) corresponds to the V_{IN} that makes the resistance of the n-channel FET ($R_n = V_{DS}/I_{DS}$) equal to the resistance of the p-channel FET ($R_p = -V_{DS}/-I_{DS}$). Accordingly, a device resistance plot can be used to analyze the switching voltage of complementary-like inverters [30]. This method is suitable for estimating the switching region in the voltage transfer characteristics in inverters with ambipolar OFETs, because it does not restrict us to calculating the resistances in a predefined operating regime, as is done in the extraction of the mobility and threshold voltage values in ambipolar devices. Moreover, there is no proper definition of threshold voltage for these devices throughout the operation.

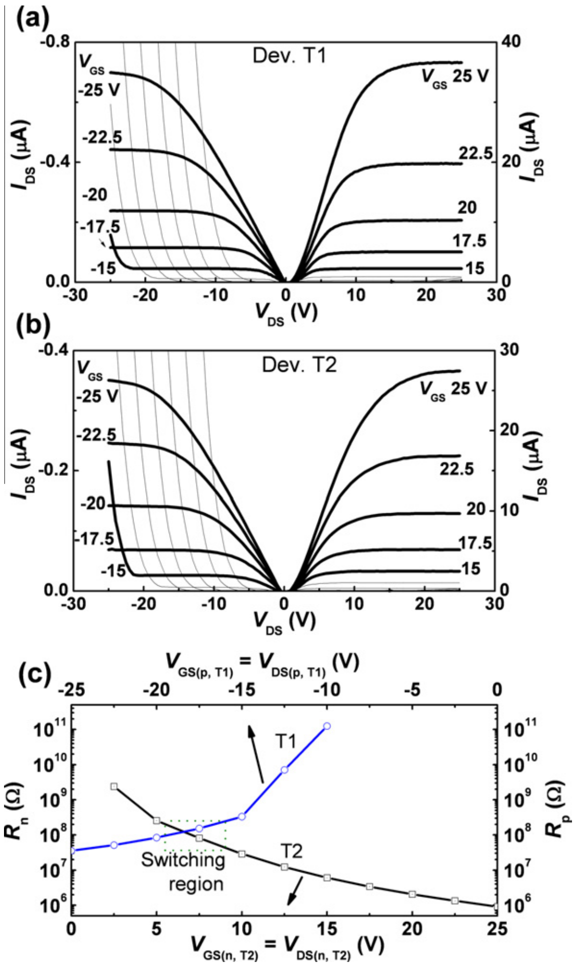

Fig. 2. Output characteristics of OFET T1 (a), and T2 (b), constituting a complementary-like inverter. (c) The resistance plot for both transistors, T1 during p-channel operation and T2 during n-channel operation, providing an estimation of the switching point.

The resistances during p- and n-channel operations can be obtained when gate and drain terminals are connected, or they can be extracted from the output characteristics of

Table 1
Summary of results for top-gate bottom-contact OFETs with NDI_2-DTP with L = 180 µm and W = 2550 or 6050 µm.

Batch	Operation	V_{DD} (V)	μ_{max} ($cm^2 V^{-1} s^{-1}$)	μ_{ave} ($cm^2 V^{-1} s^{-1}$)	V_{TH} (V)
1 (6 Dev.)	n-channel	25	1.1	0.8(±0.2)	+12.7(±0.6)
	p-channel	−25	0.01	0.009(±0.004)	−12.7(±0.4)
2 (6 Dev.)	n-channel	25	1.5	1.2(±0.3)	+13.0(±0.9)
	p-channel	−25	0.01	0.007(±0.003)	−14.2(±0.7)
3 (4 Dev.)	n-channel	25	0.8	0.7(±0.1)	+14.8(±0.8)
	p-channel	−25	0.009	0.007(±0.001)	−12.4(±0.7)

the independent OFETs at the condition of $V_{GS} = V_{DS}$ [30]. Using the same technique, the plot of the resistances of devices T1 (R_p) and T2 (R_n) are obtained. The subscript in the resistances (R_p, R_n) indicates the operation of the particular transistor in the complementary-like inverter; T1 is working as p-channel and T2 as n-channel in this case. Fig. 2c shows the values of R_p and R_n extracted from output characteristics for different values of $V_{GS} = V_{DS}$. This plot suggests the switching should occur near a V_{IN} of 7 V. Fig. 3a and b shows the voltage-transfer characteristics and DC gain of a representative complementary-like inverter fabricated with ambipolar OFETs T1 and T2. As we can see in the voltage-transfer characteristics, a complementary-like inverter shows a DC output swing range of about 20 V when V_{IN} is varied from 0 to 25 V at a supply voltage (V_{DD}) of 25 V. The DC gain is obtained by differentiating V_{OUT} with respect to V_{IN}. High DC gain values of 122.8 V/V and 94.5 V/V were obtained for this inverter in the forward scan (V_{IN} varied from 0 to 25 V) and in the reverse scan (V_{IN} varied from 25 to 0 V), respectively. No hysteresis was observed between forward and reverse scans. The other inverters fabricated in the same process exhibited high gain values exceeding 90 V/V. To the best of our knowledge, these numbers are higher than the values from any other inverters based on ambipolar OFETs reported in the literature.

4. Summary and conclusions

The electrical performance of NDI_2-DTP OFETs with a CYTOP/Al_2O_3 bi-layer gate dielectric was measured. Top-gate OFETs with a solution-processed molecular bis(naphthalene diimide)-dithienopyrrole (NDI_2-DTP) derivative showed ambipolar transistor properties with an average electron mobility value of 1.2 $cm^2\ V^{-1}\ s^{-1}$ and an average hole mobility value of 0.01 $cm^2\ V^{-1}\ s^{-1}$, respectively. Complementary-like inverters comprised of top-gate ambipolar OFETs yielded very high DC gain values of more than 90 V/V (up to 122 V/V) at a supply voltage of 25 V.

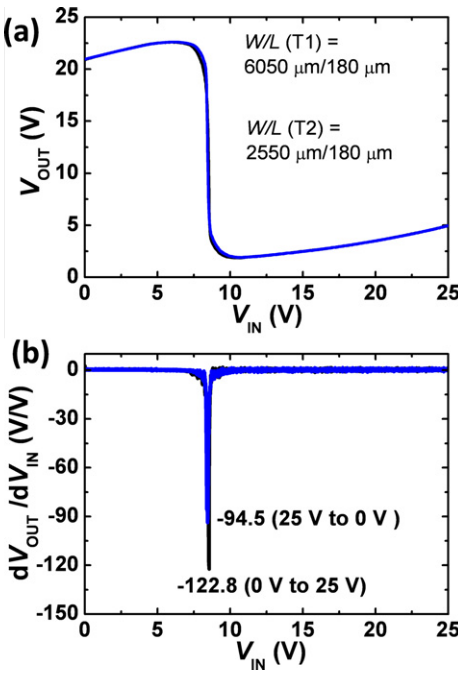

Fig. 3. (a) Hysteresis voltage transfer characteristics and (b) DC gains of a complementary-like inverter.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2012.03.029.

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