



# Controlled ambipolar charge transport of polymer semiconductors by viologen-doping for complementary-like electronic circuits

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## ABSTRACT

We report on controllable ambipolar charge transport in polymeric semiconductors by the incorporation of viologen-based molecular additives. The viologen dopants selectively contribute to an increase in the charge carrier density of the electrons while enhancing the fibril-like crystalline thin-film morphology of the polymers to provide favourable charge transport in staggered-structure organic field-effect transistors. A well-balanced ambipolar behaviour is obtained at the optimised viologen concentration in donor-acceptor conjugated polymers by conversely modulating the *p*- and *n*-channel carrier mobilities within a given active layer. Complementary-like inverter circuits are demonstrated through the application of a simple blanket coating of a viologen-doped ambipolar semiconductor, which exhibits high ideal voltage switching at around half of the applied bias, a high gain of more than 50, and sufficient noise immunity to enable various applications for printed electronics and optoelectronics.

## 1. Introduction

Recently, additive manufacturing processes have progressed considerably from the production of conventional print media, such as books, newspapers, and flexible product packaging, to the development of a variety of 2D or 3D printed electronics and optoelectronics applications [1–4]. This evolution in the printing industry is expected to contribute to the so-called “fourth industrial revolution” by realizing the ability to produce products on an on-demand basis. To realize electronic applications by additive manufacturing, it will first be necessary to develop various solution-processable active materials, such as carbon nanotubes [5], graphene [6], amorphous metal oxides [7], 2D nanomaterials [8], and  $\pi$ -conjugated organic molecules [9]. Among these materials, conjugated organic semiconductors appear to offer much greater promise than their inorganic counterparts in terms of their intrinsically soft mechanical properties, which are suitable for producing flexible/stretchable devices as well as being highly soluble in common organic solvents, allowing their application to wide range of graphic printing techniques [10]. Moreover, organic molecules can be ascribed multiple functionalities by tailoring their molecular structures and organic synthesis to engineer the charge recombination, transport, and generation characteristics of conjugated molecules for appreciably realizing a number of electronic and optoelectronic applications, such as large-area flexible displays [11], printed microprocessors [12], and

energy-harvesting devices [10].

Organic field-effect transistors (OFETs) based on solution-processable  $\pi$ -conjugated organic molecules are key elements of printed and/or flexible active components, such as active-matrix displays, wearable sensors, and driver circuits [13]. A number of low-cost printing processes have previously been used to fabricate such components, such as screen printing, inkjet printing, gravure and reverse-offset printing [14]. However, these printing processes typically have a low resolution in a range of a few tens of micrometres [2]. Although many approaches have been devised which enable the high-resolution printing of patterns and the development of high-performance printed electronic devices, it is still difficult to define sophisticated patterns especially for highly integrated electronic circuits. Notably, state-of-the-art electronic circuits are built using complementary metal oxide semiconductor (CMOS)-based architectures. Conventional CMOS circuits inevitably require multiple patterning processes including photolithography and etching to precisely define the electrodes and each *p*- and *n*-type semiconductor region. However, this approach is not ideal for developing easily fabricated electronic circuits without the complex patterning process. Therefore, an alternative electronic architecture should be considered to allow the application of roll-to-roll and low-cost printing processes.

In comparison to CMOS, complementary-like electronic circuits based on ambipolar semiconductors offer a promising solution in that

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they eliminate the need for the semiconductor patterning steps [15]. Since ambipolar semiconductors have the capability to transport both electrons and hole carriers through the same channel, a balanced charge-transport behaviour is essential to achieving the CMOS-like circuitry [14]. Recently, tailored molecular design and its successful organic synthesis have led to the development of a number of donor-acceptor (D-A) type ambipolar organic semiconducting materials. Although remarkable progress had been achieved in the field of ambipolar organic semiconductors, *p*-channel charge carrier mobilities are typically much better than those of the *n*-channel. Thus, it is necessary to attain well-balanced *p*- and *n*-channel OFET characteristics. To address such issues, many strategies have been developed, such as selective charge-injection engineering between semiconductor and source/drain contact electrodes and charge modulation by surface dipoles at the interface between the semiconductor and gate insulators [16–18]. These methods mainly utilized external effects during device operation rather than the conjugated molecule itself.

As an alternative route, the doping of organic semiconductors by incorporating molecular or ionic additives has been suggested as a means of selectively controlling the electron or hole transport properties at the same active channel layer [19,20], which induced an increase or decrease in the charge-carrier densities, that is, either the electrons or holes. A number of dopant molecules have been developed with a high electron affinity (EA, *p*-type) and low ionization energy (IE, *n*-type) that accept or donate electrons from organic semiconductors, respectively [19]. For application to CMOS-like circuits, it is necessary to develop highly efficient *n*-type dopants to improve the electron transport properties. Relative to the *p*-dopants, however, there were relatively small numbers of *n*-doping species. Moreover, the way in which those additives, when incorporated into organic semiconductors, enhance the electrical properties, as well as the corresponding doping mechanism, are still not fully understood.

In the present study, we demonstrated high-performance complementary-like organic electronic circuits by systematically controlling the *p*- and *n*-channel characteristics of D-A conjugated polymers. Viologen-based molecular additives were incorporated as the primary *n*-dopant to increase the electron density in the organic semiconductor channels. Initially, the *p*-channel-predominant conjugated polymers exhibited a significant change in their *n*-type regime, and those charge transport characteristics of ambipolar OFETs were systematically controlled by changing the doping concentrations of the active layer. When viologen-based *n*-dopants were added with an optimised molar concentration, the fibril-like crystalline morphology of the polymer film was also remarkably enhanced, leading to well-balanced *p*- and *n*-channel properties with reasonably high hole and electron mobilities. Finally, we demonstrated high-performance CMOS-like inverters using the viologen-incorporated ambipolar polymer semiconductors, which exhibited switching thresholds equal to around half the supplied bias, a high gain, and sufficient noise immunity to allow their application to highly integrated printed and flexible complementary-like circuits.

## 2. Experimental

### 2.1. Device fabrication

Top-gate/bottom-contact OFETs were fabricated on Corning XG glass substrates. As the source and drain contacts, gold (Au; 15 nm) and nickel (Ni; 3 nm) electrodes were used and patterned using a conventional photolithography process. All the devices had a channel width/length ratio of 1 mm/10  $\mu$ m. Substrates with Au/Ni-patterned electrodes were cleaned in acetone and then isopropyl alcohol in an ultrasonic bath, and finally dried by nitrogen blowing. The PDBT-co-TT was purchased from 1-Material (Dorval, Canada) and was used as-is. The PDBT-co-TT was dissolved in 1,2-dichlorobenzene (10 mg mL<sup>-1</sup>) and then mixed with 10 mM BV solution at blend ratios of 0.25, 0.5, 1.0, and 2.0 wt%, respectively. The 1,1'-dibenzyl-4,4'-bipyridinium

dichloride (benzyl viologen; BV) with a purity of 97% was purchased from Sigma-Aldrich, and a reduced solution was prepared by following method described in the literature [21,22]. Briefly, 4 mg of viologen powder was dissolved in 5 mL of deionized water (DI-H<sub>2</sub>O), followed by the addition of 10 mL of pure toluene. As a reducing agent, 80 mg of sodium borohydride was dissolved in 5 mL of DI-H<sub>2</sub>O and then added to the biphasic solution (water-toluene) and was then left overnight. As the reduction reaction proceeded, the BV was reduced by the catalytic agent and was steadily transferred from the water to the layers of the toluene. Semiconductor films were deposited by spin-coating (1500 rpm for 120 s), then annealed at 200 °C for 30 min on a hotplate in a nitrogen-filled glove box. Poly (methyl methacrylate) (PMMA) (to act as a gate dielectric layer) was dissolved in butyl acetate (80 mg mL<sup>-1</sup>), spin-coated at 2000 rpm for 60 s, and then thermal baked at 80 °C for 1 h in the same glove box. Finally, a 40 nm aluminium gate electrode was thermally evaporated onto the dielectric film through a metal shadow mask.

### 2.2. Characterization

The OFETs characteristics were measured using a Keithley 4200-SCS parameter analyser in a nitrogen-purged glove box. Ultraviolet photoelectron spectroscopy (UPS) was used to determine the Fermi level ( $E_F$ ) of the semiconducting thin films with various doping ratios. The UPS measurements were performed using an AXIS-NOVA (Kratos Inc.) at a base pressure of  $4.2 \times 10^{-9}$  Torr. The surface morphology of the PDBT-co-TT was investigated via tapping-mode AFM (Nanoscope III, Veeco Instruments, Inc.). GIWAXS patterns were measured using a multi-axis diffractometer at beamline 3C of the Pohang Accelerator Laboratory (PAL). X-rays with an energy level of 11.07 keV were directed onto the samples and the resulting diffraction patterns were recorded with a MAR165 CCD detector. The obtained scattering angles were calibrated according to the scattering vector  $q = (4\pi/\lambda) \sin(\theta)$ , where  $\lambda$  is the X-ray wavelength and  $\theta$  is the scattering angle.

## 3. Results and discussion

A diketopyrrolopyrrole (DPP)-based donor-acceptor (D-A) conjugated polymer was used to fabricate ambipolar OFETs and their complementary-like circuits. Fig. 1 shows the chemical structures of the poly (2,2'-[(2,5-bis(2-octyl)dodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo [3,4-c]pyrrole-1,4-diyl]dithiophene-5,5'-diyl-alt-thieno [3,2-b]thiophen-2,5-diyl) (PDBT-co-TT) molecule, together with the fabricated top-gate/bottom-contact (TG/BC) OFET device structure with a dielectric layer of poly (methyl methacrylate) (PMMA). Typically, DPP-based polymers consist of electron-rich and electron-deficient (D-A) moieties at the polymer backbone, which carry both the electrons and holes. In conventional coplanar devices, PDBT-co-TT typically exhibits a predominantly *p*-type semiconducting behaviour rather than ambipolar charge transport, mainly due to the blocked charge injection and/or trapping of free electrons. When we fabricated staggered TG/BC OFETs with a polymer dielectric, however, the behaviour became somewhat more ambipolar with much higher hole mobilities and relatively low electron mobilities. As can be seen in Fig. 2a and b, the output plots indicate a higher drain current ( $I_d$ ) in the *p*-channel region (at a negative drain voltage,  $V_d$ ) in comparison with those having an *n*-channel region. As listed in Table 1, the average hole and electron mobilities of OFETs based on pristine PDBT-co-TT were estimated to be 0.69 and 0.19 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. Because the PDBT-co-TT has both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of  $-5.2$  eV and  $-3.5$  eV, respectively [23], those *p*-channel-predominant OFET characteristics could be attributed to different charge-injection barriers from the same gold (Au) BC electrode (Au work function = ca.  $-4.7$  eV). To demonstrate the high-performance complementary-like electronic circuits based on the ambipolar semiconductors, it is important to obtain

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