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# Solution-Processed Ambipolar Field-Effect Transistor Based on Diketopyrrolopyrrole Functionalized with **Benzothiadiazole**

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Ambipolar charge transport in a solution-processed small molecule 4,7-bis{2-[2,5-bis(2-ethylhexyl)-3-(5-hexyl-2,2':5',2"-terthiophene-5"-yl)-pyrrolo[3,4-c] pyrrolo-1,4-dione-6-yl]-thiophene-5-yl}-2,1,3-benzothiadiazole (BTDPP2) transistor has been investigated and shows a balanced field-effect mobility of electrons and holes of up to  $\sim 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Using low-work-function top electrodes such as Ba, the electron injection barrier is largely reduced. The observed ambipolar transport can be enhanced over one order of magnitude compared to devices using Al or Au electrodes. The field-effect mobility increases upon thermal annealing at 150 °C due to the formation of large crystalline domains, as shown by atomic force microscopy and X-ray diffraction. Organic inverter circuits based on BTDPP2 ambipolar transistors display a gain of over 25.

### 1. Introduction

Organic field-effect transistors (OFETs) have potential applications in large-area displays, sensors, radiofrequency identification tags, and logic circuits with low-cost processability, and high flexibility.<sup>[1-6]</sup> OFETs using a bottom gate structure generally display hole transport only. This can be attributable to the trapping of the electrons by the hydroxyl group from the SiO<sub>2</sub> gate dielectrics.<sup>[7]</sup> Treatment of SiO<sub>2</sub> gate dielectric surfaces with organic self-assembled monolayers leads to improved performance in *n*-type OFETs fabricated from thermally evaporated small molecules or solution-processed polymer semiconducting layers.<sup>[7,8]</sup> Using a trap-free polymer gate dielectric layer, electron transport in conducting polymers has been observed, revealing a comparable field-effect mobility as holes.<sup>[9]</sup> However, for certain types of applications, ambipolar transport is required. For example, complimentary metal-oxide-semiconductor (CMOS) ambipolar transistors are preferable to increase the noise margin for logic circuits.<sup>[10]</sup> Furthermore for light-emitting transistors,[11-13] ambipolar transport is required so that the

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electric potential and the light emission zone can be controlled by the applied gate voltage.<sup>[14]</sup>

Recently, several solution-processed polymer-based OFETs using a regular bottom-gate structure with hole mobilities of ~10<sup>-1</sup> cm<sup>-2</sup> V<sup>-1</sup> s<sup>-1</sup> have been reported.<sup>[15-19]</sup> The charge-carrier mobility can be improved by tuning the intermolecular interactions between the nearest neighboring molecules,<sup>[20]</sup> which can be achieved using fused aromatic rings such as thienothiophene, cyclopentanedithiophene, and naphthodithiophene.<sup>[21-23]</sup> It is believed that the fused aromatic structures enhance  $\pi$ - $\pi$  stacking and hence induce higher molecular ordering, which

drastically improves charge transport.<sup>[16]</sup> However, conjugated polymers suffer batch-to-batch variation in terms of molecular weight and polydispersity that affect solar cell performance and field-effect mobility.<sup>[24,25]</sup>

Recently a family of soluble small organic molecules containing a diketopyrrolopyrrole (DPP) core have been synthesized.<sup>[26-33]</sup> DPP-based materials have been used in solution-processable organic solar cells showing a power conversion efficiency (PCE) up to 5.2%.<sup>[29]</sup> OFETs fabricated from soluble DPP materials show hole mobility of  $\sim 10^{-2}$  cm<sup>2</sup> V-1 s-1.[34] Incorporating fused aromatic ring moieties, the crystallinity of this type of materials can be well controlled by choosing appropriate solvents or thermal annealing, leading to desired film morphologies.<sup>[35]</sup> To the best of our knowledge, ambipolar transport based on this class of materials has not been observed previously.

Here, we report a newly synthesized bis-DPP compound, 4,7-bis{2-[2,5-bis(2-ethylhexyl)-3-(5-hexyl-2,2':5',2"-terthiophe ne-5"-yl)-pyrrolo[3,4-c]pyrrolo-1,4-dione-6-yl]-thiophene-5-yl}-2,1,3-benzothiadiazole (BTDPP2), with two electron-accepting units (DPP and benzothiadiazole, BT). The chemical structure of BTDPP2 is shown in Figure 1a. Detailed synthetic procedures can be found in the Experimental Section. The benzothiadiazole group strongly increases the electron affinity, leading to n-channel transport characteristics. We observe balanced carrier mobilities up to  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> using a bottom-gate, top electrode device architecture (Figure 1b) with appropriate top contacts. Various top electrodes with work function ( $\Phi_{
m m}$ ) from 5.1 eV (Au) to 2.7 eV (Ba) were compared to examine the effect of the injection barrier on the ambipolar transport. Using a

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Figure 1. a) Chemical structure of BTDPP2. b) FET device structure.

low-work-function Ba contact ( $\Phi_{\rm m} \sim 2.7$  eV), the drain–source currents of holes and electrons are both enhanced by more than one order of magnitude compared to OFETs with Al and Au contacts. Both the hole and electron mobilities increase from 10<sup>-4</sup> to 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with increased the annealing temperature up to 150 °C. Atomic force microscopy (AFM) shows a transition of the BTDPP2 film morphology from a fiber-like (as-cast) to crystalline-like features (above 200 °C). X-ray diffraction (XRD) measurements on BTDPP2 films prove the formation of crystalline and close intermolecular packing upon thermal annealing. Organic complementary inverters using BTDPP ambipolar OFETs show effective inversion of the input signals operating in both the first and third quadrants. Gains exceeding 25 have been achieved as a result of balanced transport properties.

#### 2. Results and Discussion

We first study the effect of thermal annealing on BTDPP2 film morphology and on the charge transport in OFET devices utilizing gold top contact. BTDPP2 films were annealed for 30 min at different temperatures inside a nitrogen glovebox. **Figure 2**a shows the saturation drain current with  $V_d = \pm 60$  V as a function of gate bias upon various annealing temperatures (*T*). We observe the lowest drain current ( $I_d$ ) from the as-cast BTDPP2 films. The current increases with increasing annealing temperature up to 150 °C. This enhancement holds both for the hole and electron currents, while the leakage currents are



nearly unchanged. With further increase in annealing temperature to 200 °C,  $I_d$  dramatically drops below that of the device annealed at 120 °C.  $V_g$ (min), defined by the gate voltage for the crossover point of the minimal drain current under electron accumulation, slightly shifts towards a lower voltage when annealed due to the change of the fixed charges at the interface. In contrast, the OFET operated in the hole-accumulation regime shows a random variation of  $V_g$ (min). Mobilities were calculated using the standard FET equation under saturation regime (Equation 1),

$$\mu_{\rm sat} = \frac{2L}{WC_{\rm i}} \left(\frac{d\sqrt{I_{\rm d}}}{d\,V_{\rm g}}\right)^2 \tag{1}$$

where  $\mu_{sat}$  stands for the field-effect mobility at saturation regime,  $C_i$  for the area capacitance of the gate dielectrics, and L/W for channel width to length ratio, the saturation mobility  $\mu_{sat}$  of BTDPP2 is calculated and plotted as a function of annealing *T* (Figure 2b).

The  $\mu_{sat}$  of the hole and electron are both in the range of ~10<sup>-4</sup> to 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Except for the devices annealed at 150 °C, the hole FET mobility of 4 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> is almost the same for the as-cast and annealed films and it is lower than that of the electron mobility by a factor of two. The FET mobility

is almost constant when  $T \leq 120$  °C, suggesting that the film morphology does not change when annealed at such temperatures. The sharp increase of  $\mu_{sat}$  up to  $2.1 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> when annealing temperature increases from 120 °C to 150 °C may indicate an improved film morphology and/or molecular packing. Under different annealing temperatures, all BTDPP2 transistors demonstrate balanced hole and electron carrier mobilities.

To further understand the transport results observed above, AFM was employed to probe change in surface morphology as a functional of thermal annealing temperature. Topographic images of the as-cast and annealed films are shown in Figure 3 with a scan size of 2  $\mu$ m  $\times$  2  $\mu$ m. The ascast film exhibits continuous fiber-like features, similar to what has been observed on other DPP derivatives.<sup>[34]</sup> Upon thermal annealing, the fiber-like structures gradually evolve into a particle-like structures showing sharper boundaries. Compared to the recently reported morphology of 2,5-di-nhexyl-3,6-bis(5"-n-hexyl[2,2';5',2"]terthiophen-5-yl)pyrrolo[3,-4-c]pyrrole-1,4-dione (DHT6DPPC6) films,<sup>[34]</sup> which displays large crystalline domains upon annealing at 150 °C, large crystalline domains of BTDPP2 films were only observed at higher annealing temperatures (240 °C). The average size of these domains is around 0.2  $\mu$ m  $\times$  1  $\mu$ m. Figure 3f shows the surface roughness as a function of annealing temperature. The roughness of the as-cast film decreases from 3.3 nm to 0.5 nm when annealed at 150 °C and inversely increases to 2.5 nm when T = 240 °C where large crystalline domains are formed. The highest mobility value is observed from films with small

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**Figure 2.** a) Saturation transfer characteristics of BTDPP2 FETs upon different annealing temperature using Au top contact. b) BTDPP2 carrier mobility as a function of annealing temperature.

domains and low surface roughness (150 °C). Large domain formation at 240 °C lead to discontinuous grain boundaries, which are detrimental to charge transport, and hence the carrier mobility decreases from  $2.1 \times 10^{-3}$  to  $1.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for holes and from  $2.1 \times 10^{-3}$  to  $3.5 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for electrons.

From AFM images, one can only probe the surface morphology. To probe change in the internal morphology as a function of annealing temperature, we performed XRD with the normal-to-surface mode and extracted the intermolecular spacing (d-spacing) of BTDPP2 films. Figure 4a shows the XRD spectra of as-cast and thermal annealed BTDPP2 films. There is no XRD peak observed for the as-cast film. The  $2\theta$  XRD peak appears at 6.2 degrees for the BTDPP2 film annealed at 120 °C, which shifts to 6.33 degrees for films annealed at 150 °C and further to 4.63 degrees when annealed at 200 °C, and 240 °C, respectively, implying that the intermolecular spacing becomes closer. The intensity of the XRD signals increases with increasing annealing temperature, indicative of the enhanced film crystallinity. For the films annealed at 120 °C and 150 °C, the XRD peak intensities are quite weak, indicating a disorder structure consistent with AFM images shown in Figure 3a-c. The *d*-spacing was calculated using Bragg's law,  $\lambda = 2d \sin \theta$ , where  $\lambda$  is the X-ray wavelength, and plotted in Figure 4b for various annealing conditions. When annealed at 150 °C, the *d*-spacing abruptly decreases from 16.5 Å to 13.95 Å and remains nearly unchanged at

higher annealing temperatures. This result helps explain why thermal annealing at 150  $^\circ C$  leads to highest hole and electron mobilities.

Next, we explore the use of low-work-function metal electrodes on the OFET performance. One of the advantages of applying bottom-gate, top-electrode device geometry is the great flexibility to utilize different metal contacts by which the injection barriers can be tuned. The OFET transfer curves using Au ( $\Phi_{\rm m}$  = 5.0 eV), Al ( $\Phi_{\rm m}$  = 4.3 eV), Ca ( $\Phi_{\rm m}$  = 3.0 eV), and Ba ( $\Phi_{\rm m}$  = 2.7 eV) contacts are compared in Figure 5. Figure 5a shows the electron current  $I_d$  at low drain bias  $V_d$ . Clearly  $I_d$ increases when the work function is lowered. This is attributed to the reduced electron injection barrier of Ba and Ca, leading to an Ohmic contact with the LUMO of BTDPP2 (3.7 eV from cyclic voltammetry). Surprisingly, the transfer characteristics of Ba OFETs display a more ambipolar feature compared to those with Au and Al contacts. To further understand this observation, the electron and hole currents in the saturation regime are compared in Figures 5b and 5c with,  $V_d = \pm 60$  V. Under the same carrier concentration induced by the gate dielectrics, the lowered electron injection barrier with Ba or Ca contacts results in higher drain currents in the first quadrant. Interestingly, the hole current in the third quadrant using Ba electrode is also much higher, leading to symmetric transfer characteristics. Under a large drain bias, the strong electric field leads to a pronounced Schottky barrier lowering and hence facilitates the carrier injection both for the electrons and holes. In contrast to unipolar OFETs, the electric potential in ambipolar OFETs reaches a minimum at some point far from either the drain or source electrodes as the gate bias approaches that applied to the drain. Thus, the drain current at saturation regime actually comprised of both types of charge carriers, similar to a p-njunction. Using low-work-function contacts, the enhancement of the electron injection upon high drain bias helps attract more holes injected from the counterpart electrode. This is the main reason that the drain current of the Ba devices under both the hole and electron accumulations is large compared to the devices using Al or Au electrodes. The carrier mobility with different top electrodes is summarized in Table 1. BTDPP2 demonstrates balanced saturation FET mobilities ranging from  $10^{-4}$  to roughly  $1 \times 10^{-2} \mbox{ cm}^2 \mbox{ V}^{-1} \mbox{ s}^{-1}.$  The difference between the hole and electron mobility is low and insensitive to the electrode used. Utilizing a low-work-function Ba contact facilitates electron injection into BTDPP2 increasing not only the electron, but hole mobility when operating the OFETs in the saturation regime. The hole and electron mobilities are enhanced by one order of magnitude compared to those using Au or Al electrodes.

In inorganic FETs, the threshold voltage  $V_{\rm th}$  refers to the onset of strong inversion. Below  $V_{\rm th}$ , since the conduction channel is totally depleted, there should ideally be no current flowing from the drain to the source.<sup>[36]</sup> In contrast, organic FETs work in accumulation and the current in an inversion regime is hardly attainable.<sup>[37]</sup> Thus, defining the  $V_{\rm th}$  in organic FETs is difficult as already addressed by Horowitz.<sup>[38]</sup> Although classical MOSFET equations are good approximations for describing the  $V_{\rm th}$  in OFETs, these equations neglect the dependence of the carrier mobility by the carrier concentration and electric fields.<sup>[39]</sup> To examine the  $V_{\rm th}$  of BTDPP2





Figure 3. 2  $\mu m$   $\times$  2  $\mu m$  AFM topographic images of BTDPP2 films prepared at different conditions: a) as-cast, annealed at b) 120 °C, c) 150 °C, d) 200 °C, and e) 240 °C. f) RMS film roughness versus annealing temperature.

OFETs, impedance measurements were performed on the metal-insulator-semiconductor (MIS) diode prepared by the same active layers. For this measurement, charge carriers in BTDPP2 films were accumulated or depleted by sweeping the gate voltage  $(V_g)$  leading to a different bulk capacitance, C. Under a certain  $V_g$ , C is minimized when the charge carriers are entirely depleted. This given  $V_{\rm g}$  is a fingerprint of flat-band condition and can be considered the  $V_{\rm th}$ . Figure 5d shows the C of the BTDPP2 MIS diode as a function of gate bias. Using Ba and Ca top contact, C strongly decreases with the gate bias from 10 V to 6 V, giving rise to a minimal value of 0.73 nF for C when  $V_{\rm g}$  =  $V_{\rm th}$  = 5 V. Conversely, using Au contact the capacitance exhibits less pronounced changes and the value of *C* at large positive bias lags behind that of devices using Ba and Ca contacts. This can be explained by the difficulty of electron injection from Au, as compared to that from low-work-function metals. As a result the charge accumulation is weaker. Importantly, the  $V_{\rm th}$  of ~5 V determined

by impedance analysis agrees well with the results extracted directly from the transfer characteristics (Figure 5) under saturation regime using the following equation:

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$$\frac{V_{\rm d}}{2} = V_{\rm g}({\rm min}) - V_{\rm th} \tag{2}$$

where  $V_{\rm g}({\rm min})$  is the gate voltage for inflection point of  $I_{\rm d}$ . The relatively low  $V_{\rm th}$  and equivalent mobility both demonstrate well-balanced, ambipolar transport in BTDPP2 transistors.

Lower electron injection barriers observed using Ba electrodes should result in low contact resistance ( $R_C$ ).  $R_C$  in an OFET describes the potential drop across the contacts, which causes a voltage loss for an effective voltage on transport channel from the fully applied drain-source bias.<sup>[40]</sup> In a staggered, bottom-gate configuration, the charge accumulation regime is formed opposite to the top drain-source contacts and it is found that  $R_{\rm C}$  shows a weaker dependence on the injection barrier than in the coplanar geometry.<sup>[41]</sup> Next, we study the contact resistance and channel length dependence of the BTDPP2 charge transport at a low drain-source bias of  $V_d = 11$  V (linear regime). The OFET transfer curves using a Ba/Al top contact are shown in Figure 6a using various channel lengths. The applied drain bias of 11 V is much lower than the gate bias to ensure that the majority of carriers in the conduction channel are electrons and the OFETs operate in a unipolar mode. At high  $R_{\rm C}$ , one can observe a strong suppression and even sign reversal of the drain current at the linear regime. From Figure 6a, with  $V_d = 11$  V, the drain current clearly increases as the gate bias exceeds 40 V. It

also scales with the channel length ranging from 40 to  $100 \,\mu m$ . This is a the signature of an Ohmic contact for electron injection and thus the  $R_{\rm C}$  for the electron injection is small. Linear electron current using Al or Au top electrode is hardly attained with large channel lengths. When applying a large enough drain voltage (60 V), the devices using Al contacts show electron transport with a large channel length (100 µm) while the overall magnitude is much lower than the Ba devices, by roughly one order of magnitude ( $I_d = 10^{-7}$  A when  $V_g = 60$  V, see Figure 1S, Supporting Information). From Figure 6a, the hole current under linear regime using Ba contacts is not measurable for different channel lengths. This is because the hole injection barrier under linear regime is still quite high due to the low horizontal electric field. Hence, the holes can not be easily injected over a relatively large energetic barrier considering the difference between the Ba work function (2.7 eV) and the highest occupied molecular orbital (HOMO) of BTDPP2 (~5.0 eV from cyclic voltammetry). Figures 6b and 6c show the





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**Figure 4.** a) XRD patterns of as-spun and annealed BTDPP2 films. b) *d*-spacing of the molecular packing for the RMS film roughness as a function of annealing temperature.

ambipolar transfer curves with  $V_d = \pm 60$  V for the electron and hole accumulation, respectively. The drain bias is high enough to overcome the hole injection barrier and the transfer curves exhibit a transition at  $\pm 30$  V, a signal of the ambipolar behavior. Using Equation 1 and the OFET formula in the linear regime expressed by Equation 3,

$$\mu_{\rm lin} = \frac{L}{WC_{\rm i} V_{\rm d}} \frac{d I_{\rm d}}{d V_{\rm g}} \tag{3}$$

where  $\mu_{\text{lin}}$  is the FET mobility at linear regime, the electron and hole mobility are calculated and plotted as a function of channel length *L* (Figure 6d). Generally, if the  $R_{\text{C}}$  is the cause of the voltage drop in an OFET, the linear mobility exhibits an asymptotic dependence on *L*. The mobility should greatly increase with larger *L* and gradually saturate at certain channel length, where the bulk resistance dominates the total channel resistance. The higher FET mobility with a larger *L* is ascribed to the larger bulk resistance as proportional to *L* and the  $R_{\text{C}}$  becomes less dominant. From Figure 6d, this trend is invisible and the carrier mobility increases only from  $8 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> to  $1.6 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, when *L* is increases from 40 to 100 µm. This further confirms that  $R_{\text{C}}$  in the Ba electrode devices is negligible.

Lastly, due to the balanced carrier mobilities observed in BTDPP2, we attempt to fabricate organic inverters based on two identical BTDPP2 OFETs. The equivalent circuit diagram is shown in the inset of **Figure 7a**. A highly *n*-doped Si gate electrode serves for the input voltage  $V_{\rm in}$  and one of two OFET drain electrodes is grounded while the other is constantly biased at the control voltage, denoted as  $V_{\rm dd}$ . The





(a)

**Figure 5.** Transfer curves of BTDPP2 FETs using various top electrodes at a) linear regime, b) ambipolar regime under electron accumulation, and c) ambipolar regime under hole accumulation. d) Capacitance of BTDPP2 MIS as a function of the gate bias.

two source electrodes are shorted for the output voltage  $V_{\text{out}}$ . Owing to the tunable channel conductivity of both the electrons and holes, one of the merits of ambipolar over unipolar inverters is that the device can be effectively operated in the first and the third quadrants,<sup>[42]</sup> greatly simplifying practical

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Table 1. Comparison of BTDPP2 FET mobility with different top contacts (e = elecron, h = hole).

Electrode	$\mu_{\rm lin}({ m e})~({ m cm}^2~{ m V}^{-1}~{ m s}^{-1})$	$\mu_{\rm sat}(e) \ ({\rm cm}^2 \ {\rm V}^{-1} \ {\rm s}^{-1})$	$\mu_{sat}(h) (cm^2 V^{-1} s^{-1})$
Al	$4 \times 10^{-4}$	$3 \times 10^{-4}$	$1.3  imes 10^{-3}$
Au	$5.6 \times 10^{-4}$	$1 \times 10^{-3}$	$1.4 imes10^{-3}$
Ca	$3.3\times10^{-3}$	$4.7\times10^{-3}$	N/A
Ва	$7  imes 10^{-3}$	8.1 × 10 <sup>-3</sup>	$9.5 imes10^{-3}$

CMOS circuits. From Figure 7a we find that Vout can be efficiently inverted from a low voltage of ±10 V to high voltage of ±80 V as a function of  $V_{\rm in}$  with both positive and negative signs. The inversion of the input voltage is found to be  $\pm 50$  V, half of the control  $V_{dd}$  (±100 V), nearly ideal for ambipolar inverters. With different V<sub>dd</sub>, which equals the maximum of  $V_{\rm in}$ , the voltage inversion always occurs at  $V_{\rm dd}/2$ . These results strongly suggest that the carrier mobility and turn-on voltages in BTDPP2 OFETs are equivalent. The AC response of the BTDPP2 inverters is also characterized by different wave functions with an AC magnitude of 10 V (peak to valley) (Figure S2, Supporting Information). The output signals display a 90 degree phase shift compared to the input sine or triangle signals at low frequencies (50 Hz). Using dV<sub>out</sub>/  $dV_{in}$ , the inverter gain, defined as how fast an input voltage can be inverted are shown in Figure 7b. Noticeably, the gains exceed 25 at both the first and third quadrants, facilitated from the balanced charge transport in BTDPP2 OFETs. These values are competitive to organic inverters based on high-mobility polymers and thermally evaporated crystalline small molecules.<sup>[43,44]</sup>

#### 3. Conclusion

In summary, solution-processable ambipolar transistors fabricated from DPP-based small molecules show field-effect hole and electron mobilities of up to  $1.6 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $1.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. Balanced transport behavior in this DPP material is confirmed by equivalent electron and hole mobilities, which is independent of the work function of the top electrodes. Thermal annealing enhances the charge transport by improving film morphology and smoothness, with an optimal OFET performance obtained after annealing at 150 °C. Large crystalline domains are observed for annealing temperatures above 200 °C, hindering the charge transport due to the formation of discontinuous grain boundaries. Closer intermolecular packing of BTDPP2 films occurs when T = 150 °C, which further explains the enhanced carrier mobility. Using low work function Ba contacts, the electron injection is greatly enhanced, leading to an improvement of both the electron and hole currents at saturation regime. Organic inverters based on BTDPP2 OFETs exhibit competitive gains in excess of 25 at both the first and third quadrants, facilitated by the balanced transport properties of BTDPP2. Thus, it is possible to design solution-processed molecules with balanced electron and hole mobilities using the donor-acceptor building-block approach.





**Figure 6.** Transfer characteristics of BTDPP2 FETs using a Ba top electrode operated at a) linear regime, b) ambipolar regime under electron accumulation, and c) ambipolar regime under hole accumulation. d) FET mobility of electrons and holes as function of channel length.

Channel length (µm)

#### 4. Experimental Section

*Material Synthesis*: 5-hexyl-2,2'-bithiophene-5'-boronic acid pinacol ester and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) were purchased from Sigma–Aldrich Chemical Co. and used as received. Other chemicals and solvents were used as received from commercial sources if there was no description. The synthesis of BTDPP2 is shown in **Scheme 1**.



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**Figure 7.** a) Transfer characteristics of BTDPP2 inverter. Inset: equivalent circuit as used. b) Gains of the BTDPP2 inverter under the hole and electron accumulation, respectively.

Conditions: i) 2,1,3-Bnezothiadiazole-4,7-bis(boronic acid piancol ester),  $Pd_2(dba)_3$ ,  $HP(tBu)_3BF_4$ ,  $K_3PO_4$ , THF; ii) NBS, Chloroform; iii) 5'-Hexyl-2,2'-bithiophene-5-boronic acid pinacol ester,  $Pd_2(dba)_3$ ,  $HP(tBu)_3BF_4$ ,  $K_3PO_4$ , THF.

2, 5-Bis(ethylhexyl)-3-(5-bromo-thiophene-2-yl)-6-(thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione, 1: To a solution of 2,5-bis(2-ethylhexyl)-3,6-di(thiophene-2-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (2.3 g, 7.8 mmol)<sup>1</sup>

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in 55 mL of chloroform, N-bromosuccinimde (NBS) (0.92 g, 5.2 mmol) was added. The reaction solution was stirred for 5 hours at room temperature in the dark. After adding more chloroform, solution was washed with waster and dried over magnesium sulfate. After solvent was removed under reduced pressure, the crude product was purified by column chromatography on a silica gell with chloroform/hexane from 1/1 to 2/1 ( $\nu/\nu$ ) to afford 1 (1.5 g, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.89 (d, 1H, J = 2.8 Hz), 8.62 (d, 1H, J = 3.6 Hz), 7.63 (d, 1H, J = 4.8 hz), 7.26 (d, 1H, J = 4.0 Hz), 7.21 (d, 1H, J = 3.6 Hz), 3.88–4.05 (m, 4H), 1.84 (bs, 2H), 1.20 –1.36 (m, 16H), 0.82–0.89 (m, 12 H).

4, 7-Bis {5-[2, 5-bis (2-ethylhexyl)-6-(thiophene-2-yl)-pyrrolo[3, 4-c]pyrrole 1,4-dione-3-yl]thiophene-2-yl]-2,1,3-benzothiadiazole, 2: To a mixture of 2.1.3-benzothiadiazole-4.7-bis(boronic acid pinacol ester) (0.23 g. 0.60 mmol), 1 (0.90g, 1.5 mmol), tri(dibenzylidene-acetone)palladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>) (0.027 g, 0.030 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.052 g, 0.18 mmol), and potassium phosphate (1.0 g, 4.8 mmol), a degassed THF/water (20 mL/2 mL) was added. After stirring under argon at 50 °C overnight, the reaction mixture was poured into water. The crude product was extracted by chloroform and dried over magnesium sulfate. After evaporate solvent, the crude product was purified by column chromatography on a silica gel with from pure chloroform to 1% acetone in chloroform to afford 2 (0.5 g, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.13 (d, 2H, l = 4 Hz), 8.96 (d, 2H, J = 4Hz), 8.17 (d, 2H, J = 3.6 Hz), 8.01 (s, 2H), 7.63 (d, 2H, J = 5.2 Hz), 7.29 (d, 2H, J = 4Hz), 4.04-4.16 (m, 8H), 2.00 (bs, 2H), 1.90 (bs, 2H), 1.25-1.46 (m, 32H), 0.86-0.98 (m, 24H).

4, 7-Bis {5-[2, 5-bis (2-ethylhexyl)-6-(5-bromo-thiophene-2-yl)-pyrrolo[3, 4-c] pyrrole-1, 4-dione-3-yl]thiophene-2-yl]-2, 1, 3-benzothiadiazole, 3: NBS (0.16 g, 0.88 mmol) was added to a solution of 2 (0.50 g, 0.42 mmol) in 40 mL of chloroform. The solution was stirred overnight in the dark. The solution was diluted with additional chloroform and washed with water. After evaporate solvent under reduced pressure, the crude product was purified by column chromatography on a silica gel with chloroform/hexane from 5/1 to 20/1 ( $\nu/\nu$ ) to yield 3 (0.35 g, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.11 (d, 2H, J = 2.8 Hz), 8.70 (d, 2H, J = 4.0 Hz), 8.07 (d, 2H, J = 4.0 Hz), 7.89 (d, 2H), 1.28–1.44 (m, 32H), 0.87–0.97 (m, 24H).

4, 7-Bis{2-[2,5-bis(2-ethylhexyl]-6-(5-hexyl-2,2':5',2''-terthiophene-5''-yl)pyrrolo[3,4-c]pyrrolo-1,4-dione-3-yl]-thiophene-5-yl]-2,1,3-benzothiadiazole, 4: Degassed THF/water (10 mL/1 mL) was added to a mixture of 3 (0.35 g, 0.26 mmol), 5-hexyl-2,2'-bithiophene-5'-boronic acid pinacol ester (0.24 g, 0.64 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.012 g, 0.013 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.023 g, 0.79 mmol), and potassium phosphate (0.44 g,



Scheme 1. Synthetic Route for 4 (BTDPP2).

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2.1 mmol). After stirring overnight under argon at 60 °C, the reaction mixture was poured into water. The crude product was extracted with chloroform and purified by column chromatography on a silica gel with from chloroform/hexane 5/1 ( $\nu/\nu$ ) to pure chloroform to obtain 4 (0.22 g, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.03 (s, 2H), 8.97 (s, 2H), 7.90 (s, 2H), 7.71 (s, 2H), 7.06 (d, 2H, J = 3.6 Hz), 6.98 (d, 2H, J = 4.0 Hz), 6.88 (d, 2H, J = 3.2 Hz), 6.84 (d, 2H, J = 3.6 Hz), 6.58 (d, 2H, J = 3.2 Hz), 3.78–4.05 (m, 8H), 2.68 (t, 4H, J = 7.2 Hz), 1.82–1.98 (m, 4H), 1.61 (m, 4H), 1.21–1.50 (m, 44H), 0.86–1.02 (m, 30H). Anal. Calcd. for C<sub>94</sub>H<sub>112</sub>N<sub>6</sub>O4<sub>S</sub><sub>9</sub> (%): C, 67.26; H, 6.73; N, 5.01 Found: C, 66.78; H, 6.69; N, 5.11.

Device Fabrication and Characterization: N<sup>++</sup> Si wavers from Silicon Quest International were used for the bottom gate electrode with 150 nm of SiO<sub>2</sub> layer as the gate dielectric, leading to a capacitance of  $\sim$ 2.3  $\times$  10<sup>-4</sup> F m<sup>-2</sup>. Prior to casting the BTDPP2 active layer, the substrates were sonicated sequently with acetone, and propan-2-ol, 2-propanol and then baked on a hotplate at 140 °C for 1 hour. Following with 30 min of UV-ozone treatment, the substrates were then transferred into a nitrogen purged glove box and passivated with diluted octadecyltrichlorosilane solution in hexane (0.1% vol). BTDPP2 was dissolved in chloroform at a concentration of 6 mg mL and stirred on a hotplate at 60 °C. Filtered through a PTFE filter with 0.45 µm pore size, the films were deposited from BTDPP2 solution at a spin-speed of 2000 RPM resulting in ~50 nm film thickness. Finally 90 nm Au, or Al top contacts were thermally evaporated under a vacuum lower than  $5 \times 10^{-7}$  torr through a shadow mask (2 mm channel width and 40~100  $\mu$ m channel length). For low work function metals, 5 nm Ba or Ca was evaporated and immediately capped with 100 nm of Al. The samples were tested in a LakeShore probe station under 10<sup>-6</sup> mBa. A Keithley 4200 semiconductor parametric analyzer was used for the OFET and inverter characterizations. Impedance of the metal-insulator-semiconductor diodes was recorded using a Solartron SI 1260 impedance/gain-phase analyzer. The capacitance was obtained by sweeping the gate voltage while keeping the top electrode grounded.

For morphological studies the same BTDPP2 films were used to the OFET active layers. The tapping mode AFM images were captured by a Veeco MultiMode 8 scanning probe microscope under nitrogen atmosphere. Thin-film XRD spectra were measured on device architectures of Si/SiO<sub>2</sub>/BTDPP2 using an X'Pert Phillips Material Research diffractometer. Samples were scanned at 45 kV and 40 mA with a scanning rate of 0.004 degree per second, and Cu K $\alpha$  radiation (wavelength  $\lambda = 1.5405$  Å). In the  $2\theta$ - $\omega$  scan configurations each film was scanned from 4 to 30  $2\theta$ .

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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