This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

www.rsc.org/chemcomm
Solution-grown single-crystalline microwires of a molecular semiconductor with improved charge transport properties

Akshaya K. Palai,†4 Jihee Lee,†4 Tae Joo Shin,† Amit Kumar,‡ Seung-Un Park,‡ Seungmoon Pyo*‡

Preparation and structural analysis of highly ordered single crystalline wires of diketopyrrolopyrrole (DPP) molecular semiconductor grown through a solution process is reported, and the static/dynamic electrical response of organic electronic device using the DPP semiconductor has been analyzed.

Conjugated organic materials that can be self-assembled into nano/micro structures and easily processed from solution are useful for high performance organic field-effect transistors (OFETs). Among the various conjugated organic materials, diketopyrrolopyroles (DPPs) were recently considered as suitable materials for OFETs owing to their flexible processability and attractive optoelectronic properties. Recently, OFETs based on molecular DPPs containing alkylated thiophenes prepared by solution processes over n-octadecyltrichlorosilane (OTS)-modified Si/SiO$_2$ have been reported with a field-effect hole mobility of ~10$^{-2}$ to ~10$^{-3}$ cm$^2$/V·s. However, the use of 1D-micro/nanostructures obtained from DPP derivatives for fabricating solution-processable efficient OFETs is limited. In addition, OFETs and complementary inverters that are based on the micro/nanostructures of molecular DPP on solution-processable gate dielectric, are very rare. In this communication, we present a simple solution-based approach for the preparation of single-crystalline microwires of 2,5- dihexadecyl-3,6-bis(5-(3-hexylthiophen-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP(3HT)$_2$) (chemical structure is shown in Fig. 1). The charge transport behaviors of OFETs and complementary inverters with a solution-processable gate dielectric were investigated by measuring their static and dynamic electrical response, in addition to analyzing the structure of single crystalline DPP(3HT)$_2$ microwires using grazing-incidence X-ray diffraction (2D-GIXD) and this structure with that of DPP(3HT)$_2$ thin film. Our single crystalline microwires based organic transistor and inverter exhibit a high mobility of 0.40 cm$^2$/V·s with an on/off ratio of 10$^3$ and a high gain of 18, respectively.

Fig. 1 A schematic fabrication procedure for DPP(3HT)$_2$ microwire-based OFET (a). The OM images (b and d) (scale bar 50 μm) and AFM images (c) of a DPP(3HT)$_2$ single microwire grown on Si/SiO$_2$ (5×5 μm$^2$, scale bar 2 μm) and CL-PVP/ITO (15×15 μm$^2$, scale bar 5 μm) substrate.

The best and average $I_{DS}$- $V_{DS}$ curves of the OFETs with multiple wires are shown in Figs. S1(a-e) and Figs. S1(a-e, ES1†). The images confirm that the DPP(3HT)$_2$ wires lie between the electrodes of the OFETs. The OM and AFM images of one (Fig 1b-c) and two (Fig S1a-c, ES1†) DPP(3HT)$_2$ wire based OFETs on Si/SiO$_2$ substrate are shown. The output ($I_{DS}$ - $V_{GS}$) and transfer ($I_{DS}$ - $V_{GS}$) curves of the OFETs with multiple wires show typical $p$-type charge transport behavior as depicted in Figs. S2a and b (ESI†). The best and average field-effect hole mobility ($μ_h$) of the device was 0.40 and 0.12 cm$^2$/V·s, almost 200 and 60 times higher than that of DPP(3HT)$_2$ film based devices, respectively and even higher compared to the reported values of DPP crystal based OFETs. Average values of $μ_l$, $V_{th}$, $I_{on}/I_{off}$, and $ss$ as calculated from 13 devices are ~0.12 cm$^2$/V·s, 7.00 V, 2.03 × 10$^3$ and 10.60 V/dec, respectively. We also successfully fabricated OFETs with a single DPP(3HT)$_2$ wire, the output and transfer characteristic curves of...
which are shown in Figs S2c and d (ESI\textsuperscript{1}), respectively. The maximum values achieved of \( \mu_{\text{fb}} \), \( V_{\text{th}} \), \( I_{\text{on}}/I_{\text{off}} \), and ss were \(-0.15\) cm\(^2\)/V·s, 7.70 V, 9.93 \times 10\(^3\) and 5.50 V/dec, respectively. Detailed device performance parameters are summarized in Table S1 (ESI\textsuperscript{1}).

In order to investigate the electrical behavior of the DPP wire on polymer gate dielectric, essential for flexible organic devices, DPP(3HT)\(_2\) single-crystalline wires were also grown on the CL-PVP gate dielectric, and the device’s performance was analyzed. The OM and AFM images of the single (Fig 1d-e) and four (Fig S1d-e, ESI\textsuperscript{1}) DPP(3HT)\(_2\) wire-based OFETs with CL-PVP are shown. The characteristic curves of devices with multiple wires are shown in Fig. S3a and b (ESI\textsuperscript{1}), respectively. Such OFETs showed typical p-channel behavior and a moderate saturation behavior. The maximum values achieved of \( \mu_{\text{fb}} \), \( V_{\text{th}} \), \( I_{\text{on}}/I_{\text{off}} \), and ss of the OFET were estimated to be \(-0.14\) cm\(^2\)/V·s, 4.3 V, 2.03 \times 10\(^3\), and 8.5 V/dec, respectively. Compared to DPP(3HT)\(_2\) thin-film based OFETs, the mobility of such OFETs increased by \(-75\) (from best mobility) and \(-25\) (from average mobility, table 1) times, which is comparable or higher to those previously reported other functionalized DPP derivatives.\textsuperscript{10}

**Fig. 2** Output (a) and transfer (b) characteristics of the OFET (L/W = 20/10.7 µm) with a single 1D-microwire of DPP(3HT)\(_2\) on CL-PVP gate dielectric.

In addition, air stability of the devices was investigated as shown in Fig. S4 (ESI\textsuperscript{1}) by measuring device’s (having 4 wires) performance after storage for 65 days in air. Upon such air storage, mobility decreased moderately to \(-0.01\) cm\(^2\)/V·s, but still showed good p-channel properties. We also successfully fabricated a device with a single DPP(3HT)\(_2\) wire grown on CL-PVP. The device’s characteristic curves are shown in Figs 2a and b. The maximum achieved values of \( \mu_{\text{fb}} \), \( V_{\text{th}} \), \( I_{\text{on}}/I_{\text{off}} \), and ss are \(-0.08\) cm\(^2\)/V·s, \(-15.2\) V, 1.52 \times 10\(^3\), and 20.5 V/dec, respectively. We found that the performance of devices based on crystalline wires were much better than that of film-based devices. In order to correlate the structures of DPP(3HT)\(_2\) in its thin-film and crystalline wire forms with device performance, two-dimensional grazing incidence X-ray diffraction (2D-GIXD) experiments were performed (detailed in ESI\textsuperscript{1}). Fig. 3a and b show the GIXD images of DPP(3HT)\(_2\) wire and 50-nm thick film on CL-PVP/ITO substrate, respectively. In Fig. 3a, characteristic spot-like strong diffractions are clearly seen, strongly suggesting the single crystalline nature of wire. On the other hand, the GIXD patterns of the thin-film exhibit very broad and diffused peaks as in Fig. 3b, indicative of either amorphous-like features or a crystalline nature with low crystallinity. Fig. 3b shows extra diffraction peaks at an angle of \(-69^\circ\) from the surface normal. (the dotted ellipsoids in Fig. 3b). Out-of-plane 1D-GIXD profiles at \( q_{\text{xy}} = 0 \) (\( q_x \)-profiles) are plotted in Fig. 3c.

![Fig. 3](image)

**Fig. 3** 2D-GIXD images of DPP(3HT)\(_2\) (a) microwire and (b) 50 nm-thick film on CL-PVP/ITO substrate. The \( q_x \)-profiles extracted from (c) measured GIXD data and (d) simulated 2D-GIXD images.

The \( q_x \)-profile of a wire shows two distinct peaks at \( q_x = 0.2111 \) and 0.4215 Å\(^{-1}\), which can be assigned as the 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) order diffraction peaks associated with a lamellar structure with 29.8 Å layer spacing. Thin-film shows diffraction peaks at \( q_x = 0.1961, 0.3932, 0.5894, 0.9890, \) and 0.2811 Å\(^{-1}\) (indicated by * in Fig. 3c). These peaks (assigned as \( h00 \)) diffractions) are attributable to the 1\(^{\text{st}}\) and higher order peaks of a lamellar structure with 32.0 Å interlayer spacing. In order to understand these diffraction patterns, the molecular structure of DPP(3HT)\(_2\) was considered. A DPP(3HT)\(_2\) molecule consists of rigid central DPP conjugation unit about 18 Å-long, and long alkyl side of length 7.6 Å (C6) and 20.3 Å (C16) attached perpendicularly to the conjugation unit. The fully extended molecular length along the long side alkyl chains is calculated to be about 45 Å. So, when a DPP(3HT)\(_2\) molecule is regularly aligned on the surface, in which long side alkyl chains are normal to the surface and the edge of conjugation unit is parallel to the surface (see, a schematic model in Fig. 3a, inset, enlarged one in Fig. S5, ESI\textsuperscript{1}), its single layer spacing is 45 Å. However, if the molecule is slightly tilted (less than 5°) on the surface and side long alkyl chains are interdigitated between the lower and upper layer by about 13 ~ 15 Å (3/4th the size of the long side alkyl chain), then the distance between the layers will be 30-32 Å, an observation consistent with the lamellar spacing of 29.8 and 32.0 Å observed for wire and thin-film, respectively.

As mentioned above, thin-films show extra diffractions at \( q_x = 0.381, 0.761 \text{ Å}^{-1}, \) and 0.2811 Å\(^{-1}\). The first two peaks are attributable to the 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) order peaks of 16.5 Å for a regular structure at the angle of 69° from the surface normal, while the third diffraction corresponds to an interlayer spacing of 22.4 Å for layer structure. These results suggest that a conjugation unit of DPP(3HT)\(_2\) molecule is oriented at an angle of 69° to the central rigid backbone (see a schematic model on the right in Fig. 3b, inset, enlarged one in Fig. S5, ESI\textsuperscript{1}) such that the vertical and lateral interlayer spacing values are 22.4 Å and 16.5 Å, respectively. Based on the abovementioned results of structural analysis, it can be inferred that a conjugation unit in DPP(3HT)\(_2\) films exhibit both parallel and pseudo-perpendicular (\(-69^\circ\)) geometry to the surface, while wires show only one parallel geometry. Considering the structural characteristics of DPP(3HT)\(_2\) wires and thin-films, it can be inferred that wires with single crystal-like features will
inevitably lead to much efficient charge transport compared to thin-film with amorphous-like feature and two mixed crystal structures. In practice, this favorable molecular packing of DPP(3HT)$_2$ is reflected in terms of the high hole carrier mobilities for highly ordered wire-based OFETs as opposed to the thin-film based OFETs (Table S1, ESI†). Furthermore, in order to confirm our interpretation of the parallel geometry of DPP(3HT)$_2$ wires, their 2D-GIXD patterns were calculated by means of the software ANAELU$^{11}$ as shown in Fig. 3d, based on the characteristics of a triclinic unit cell with $a = 30.06$ Å, $b = 10.89$ Å, $c = 5.06$ Å, $\alpha = 79.3^\circ$, $\beta = 88.3^\circ$, and $\gamma = 88.7^\circ$. It is clearly seen that the measured diffraction pattern for wires is consistent with the calculated diffraction pattern, with the exception of spot-like features (Fig S6, ESI†).

A simple logic circuit, a complementary inverter (inset of Fig. 4b), was constructed by combining $p$- (DPP(3HT)$_2$) wire and $n$-channel (PTCDI-C$_8$ wire, inset of Fig. 4a) OFETs with CL-PVP gate dielectric (Fig S7, ESI†). Figs. 4a and b show the typical voltage transfer curve ($V_{IN}$ vs $V_{OUT}$) and the corresponding gain from 0 to 60 V at two $V_{DD}$S (40 V and 60 V). The inverter shows good inversion with small hysteresis in air with a maximum gain ($dV_{OUT}/dV_{IN}$), which is the switch speed of the device, of 18 at $V_{IN}$ = 35 V. The high gain and the lower hysteresis of the device in air indicates DPP(3HT)$_2$ wires could be used in more complex logic circuits. We also measured the dynamic response characteristics of the inverter at an input frequency of 1 Hz, at $V_{DD}$ of 60 V (Fig. 4c) and 80 V (Fig. 4d). It was found that the inverter achieves good inversion to $V_{IN}$ for both values of $V_{DD}$ (60 V and 80 V).

We successfully fabricated DPP(3HT)$_2$ wire-based OFETs and complementary inverters, and analyzed the performance of these device. Crystalline wire-based OFETs showed much better device performance than did thin-film based devices owing to the high homogeneity of crystal structure in DPP(3HT)$_2$ wires. That is, while the wire exhibits only one parallel geometry, the thin-film exhibits both parallel and pseudo-perpendicular ($\sim 69^\circ$) geometries leading to the high difference in the charge transport properties of the respective devices. Finally, organic complementary inverters based on DPP(3HT)$_2$ ($p$-channel) and PTCDI-C$_8$ ($n$-channel) wires were fabricated on polymer gate dielectric and inversion characteristics were investigated, that is the first report on 1D-microwire of molecular DPP.

This work was supported by the National Research Foundation (NRF) funded by the Korea Government (MEST) (R11-2008-052-03003, 2012R1A2A2A01045694). A.K.P. acknowledges financial support from the KU Brain Pool Program of Konkuk University.

Notes and references

†Department of Chemistry, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 143-701, Republic of Korea. Email: pyosm@konkuk.ac.kr; ‡Pohang Accelerator Laboratory, Pohang, 790-784, Republic of Korea.

‡These authors have equally contributed to this work.

Electronic Supplementary Information (ESI) available: Materials, device fabrication and characterization details. See DOI: 10.1039/c00000x/