Nanoscale Ion-Doped Polymer Transistors

Quentin Thiburce, Alexander Giovannitti, Iain McCulloch, and Alasdair J. Campbell

Nano Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.nanolett.8b04717 • Publication Date (Web): 05 Feb 2019

Downloaded from <http://pubs.acs.org> on February 10, 2019

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

Nanoscale Ion-Doped Polymer Transistors

Quentin Thiburce,[†] Alexander Giovannitti,^{‡,¶} Iain McCulloch,^{‡,¶,§} and Alasdair J. Campbell^{*,†,¶}

[†]*Experimental Solid State Physics group, Department of Physics, Blackett Laboratory, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom*

[‡]*Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom*

[¶]*Centre for Plastic Electronics, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom*

[§]*Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*

E-mail: alasdair.campbell@imperial.ac.uk

Abstract

Organic transistors with submicron dimensions have been shown to deviate from the expected behaviour due to a variety of so-called ‘short-channel’ effects, resulting in nonlinear output characteristics and a lack of current saturation, considerably limiting their use. Here, using an electrochemically-doped polymer in which ions are dynamically injected and removed from the bulk of the semiconductor, we show that devices with nanoscale channel lengths, down to 50 nm, exhibit output curves with well-defined linear and saturation regimes. Additionally, they show very large on-currents on par with their microscale counterparts, large on-to-off ratios of 10^8 , and record-high width-normalized transconductances above 10 S m^{-1} . We believe this work paves the way for the fabrication of high-gain, high-current polymer integrated circuits such as sensor

arrays operating at voltages below $|1\text{ V}|$ and prepared using simple solution processing methods.

Keywords

organic electronics, conjugated polymer, large transconductance, organic electrochemical transistor (OECT), ion gel, short-channel transistor

In a conventional organic thin-film transistor (OTFT), the channel length (L) and contact length (L_c) cannot be arbitrarily reduced without seriously affecting the electrical characteristics of the device. Indeed, as L_c decreases, the contribution of the contact resistance (R_c) towards the overall device resistance becomes increasingly important, to the point where the transistor becomes limited by the charge injection process, which can lead to parasitic effects such as a superlinear output curve at low drain voltages and a lowering of the effective mobility.^{1,2} Another major drawback is that ideal transistor behaviour requires a long channel, so that the longitudinal electric field (along the channel, between the source and drain contacts) is negligibly small as compared to the transverse electric field (perpendicular to the channel plane). As L is reduced, the drain bias-induced channel shortening after pinch-off is no longer negligible and instead of reaching a plateau, the drain current increases linearly with the drain voltage in the saturation regime. This is known as channel length modulation.³ In extreme cases, the electric field in the channel becomes two-dimensional and the channel current is dominated by a space charge-limited current that is not confined at the semiconductor/insulator interface but instead flows through the bulk of the semiconductor, yielding superlinear output curves, preventing transistor saturation and greatly reducing the on-to-off ratio and mobility.³ Thus, while OTFTs now routinely exhibit mobilities (μ) in excess of $1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, the standard for the current amorphous Si TFT technology,⁴⁻⁷ this is not sufficient to maximize the performance of submicron devices and strategies should

be devised to reduce R_c and maintain a large transverse electric field, i.e. maximize the dielectric capacitance per unit area (C_i).

Previous attempts to overcome these limitations involved the use of an ultra-thin dielectric⁸ or a self-assembled monolayer (SAM)⁹ as gate insulator to maximize C_i , selective contact doping¹⁰ of the semiconductor at the interface with the metal to reduce R_c , or a combination of these methods.¹ However, the rather complex processing required with these approaches might be inadequate to fabricate low-cost organic circuits. When a polyelectrolyte – a polymer bearing ionic groups with mobile counterions – is used as gate insulator, polymer transistors can operate below $|1\text{ V}|$ because the gate voltage is dropped in about 1 nm-thick electrical double layers (EDLs) at the interfaces independently of insulator thickness.¹¹ Such polyelectrolyte-gated EDL transistors fabricated with $L = 200\text{ nm}$ were shown to saturate, albeit with some channel length modulation.¹² However, while their potential for facile large-area and high-speed processing makes them attractive,¹³ they displayed a very small on-to-off ratio of 25, which is a critical shortcoming for practical applications.

Here, we investigate short-channel polymer transistors gated with an ion gel, a polymer electrolyte consisting of a polymer matrix containing an ionic liquid, a salt in the liquid state at room temperature that exhibits high electrochemical stability and ionic conductivity. The use of ion gels in polymer transistors was pioneered by Frisbie and co-workers, who demonstrated high-performance aerosol-jet printed ion gel-gated polymer transistors.¹⁴ However, to the best of our knowledge, previous publications only reported the use of ion gels in devices with $L \geq 1\text{ }\mu\text{m}$.¹⁵ Ion gel-gated polymer transistors operate in a similar fashion to their polyelectrolyte-gated counterparts, but when a conjugated polymer inside which ions can penetrate is employed, the transistor operates in the electrochemical mode: instead of forming an EDL at the conjugated polymer–electrolyte interface, ions induce electrochemical doping in the entire volume of the polymer film, switching it to a conductive state.¹⁶ Such devices are referred to as organic electrochemical transistors (OECTs). Thus, while the lateral and transverse component of the electric field can easily be calculated and used

to explain why short-channel EDL transistors exhibit saturating output curves,¹² the same cannot be done for OECTs. The capacitance of OECTs is three-dimensional, which results in a high projected capacitance per unit area,¹⁷ as well as a high transconductance,¹⁸ which is conventionally used as figure-of-merit in such ion-doped devices¹⁹ and given by

$$g_m = \frac{\partial I_D}{\partial V_G}, \quad (1)$$

where I_D and V_G are the drain current and gate voltage, respectively. Furthermore, the width-normalized contact resistance of ion gel-gated OECTs ($R_c W \sim 1$ to $10 \, \Omega \, \text{cm}$ for P3HT, where W is the channel width) has been shown to be orders of magnitudes lower than that of conventional OTFTs²⁰ ($R_c W$ often exceeds $10 \, \text{k}\Omega \, \text{cm}$ in OTFTs employing solution-processed conjugated polymers), though the exact reason has yet to be determined. Hence, in light of these combined attractive properties, we seek to demonstrate that ion gel-gated OECTs could be used to overcome the poor performance of short-channel polyelectrolyte-gated EDL transistors, while keeping the advantage of not necessitating additional complex processing steps (outside of contact nano-patterning) such as extensive contact engineering, gate self-alignment and vacuum-deposition of the semiconductor and dielectric with critical thickness control.

As references, long-channel ion gel-gated OECTs ($L_c = 5 \, \mu\text{m}$, $L = 10 \, \mu\text{m}$, $W = 2000 \, \mu\text{m}$) with a $15 \, \text{nm}$ -thick P3HT channel were prepared as shown in Figure 1a. A typical device (Figure 1c) exhibited a large on-current $I_D = 0.75 \, \text{mA}$, a width-normalized transconductance $g_m/W = 0.62 \, \text{S} \, \text{m}^{-1}$ and an on-to-off ratio of 10^6 , and operated at voltages of only $-1 \, \text{V}$. While a record performance was not sought in this work, these values compare well with those of state-of-the-art ion gel-gated OECTs reported by the Frisbie group,^{14,16} as well as with the devices we previously fabricated by using the same photolithographic process and the same ionic liquid incorporated in a different polymer host.²¹ The linear and saturation regimes could clearly be identified from the output characteristics (Figure 1b). The linear

Figure 1: Device architecture and long-channel device characteristics. (a) Schematic representation of the device architecture and chemical structure of the materials used: the polymer semiconductor, regioregular P3HT, the ionic liquid, P₁₄:TFSI and the polymer used to contain it and form the ion gel, PEO. (b) Output and (c) transfer characteristics and width-normalized transconductance of a microscale channel P3HT ion gel-gated OEET.

curves at low drain voltages, V_D , suggest that charge injection is not the bottleneck to device performance, while the constant current in saturation indicates negligible leakage currents through the ion gel and no channel length modulation. The total width-normalized resistance at $V_G = -0.7 \text{ V}$, obtained from the slope of the linear part of the output curve, was $R_t W = 265 \Omega \text{ cm}$. When accounting for the increase in channel resistance resulting from the much thinner P3HT layer used here, this $R_t W$ value scales well with that previously reported for 800 nm-thick P3HT ion gel-gated OEETs with the same channel length.²⁰

To investigate the short-channel behaviour, nanoscale ion gel-gated OEETs were prepared in the same manner using electron-beam lithography to downscale W , L and L_c (Figure 2a–b). The characteristics of a P3HT nanoscale ion gel-gated OEET with $L = 50 \text{ nm}$ and

Figure 2: Short-channel P3HT device. (a) Optical micrograph of a transistor channel ($L = 900 \text{ nm}$, $L_c = 1100 \text{ nm}$) showing the Au contacts prepared via electron-beam lithography, the photolithographically patterned P3HT layer and the insulating resist layer surrounding the channel. (b) SEM image of the contacts (scale bar: 500 nm), (c) output characteristics and (d) transfer characteristics and width-normalized transconductance of a device with $L = 50 \text{ nm}$ and $L_c = 550 \text{ nm}$.

$L_c = 550 \text{ nm}$ are displayed in Figure 2c–d. As can be seen, the nanoscale device exhibits on-currents comparable with microscale devices, while the on-to-off ratio is increased by two orders of magnitudes to 10^8 , which we attribute to the much smaller overlap area between the source and drain contacts and the ion gel, which dramatically reduces the magnitude of ionic displacement currents. This is contrary to the trend seen in conventional OTFTs, for which the on-to-off ratio is consistently observed to decrease at small channel lengths,^{1,3} as well as in polyelectrolyte-gated EDL transistors.¹² Impressively, g_m/W reaches 12 S m^{-1} , on par with that of organic electrochemical transistors gated with an aqueous electrolyte when accounting for the semiconductor thickness¹⁸ and, to the best of our knowledge, a record value for a solid-state polymer transistor. Linear and saturation regimes can still be clearly

identified from the output curve, with no signs of channel length modulation. This is quite a remarkable result, as one would expect strong nonlinearities to arise at small V_D and an absence of saturation at such a small channel length. The fact that ion gel-gated OEETs exhibit near-ideal current saturation for channel lengths down to 50 nm suggests that the depletion layer forming at the drain after channel pinch-off stays localized in a volume within a few nanometres of the contact, so that the ensuing channel shortening stays negligible and channel length modulation is not observed.

Figure 3: Impact of contact length. (a) Evolution of the width-normalized transconductance of P3HT nanoscale ion gel-gated OEETs as a function of the gate voltage for various values of (L, L_c) . (b) Width-normalized resistance scaling with the inverse of the contact length for the two polymers used. The dashed lines are linear fits to the data.

It was previously observed that the transconductance of depletion-mode PEDOT:PSS OEETs with short channels deviates from the expected scaling with Wd/L .²² Qualitatively, it is to be expected that such a short channel made-up of a doped polymer will require a large charge injection interface area in order for the contacts to ‘keep up’ with the large current density that can be accommodated by the channel. A full analysis of the contact resistance of our devices is admittedly needed and will be the subject of future works, although quantitative observations can already be made from the available data. Plotting the g_m/W of P3HT devices against V_G for different values of L and L_c (Figure 3.a) reveals that g_m/W clearly does not scale as $1/L$ as expected. Not only is the highest maximum value

$g_m/W = 16 \text{ S m}^{-1}$ obtained for the longest channel ($L = 900 \text{ nm}$), but about 12 S m^{-1} is measured for devices with $L = 50, 160$ and 400 nm , despite the eight-fold difference in channel length. This can be explained by considering the length of the contacts instead, which is also displayed in Figure 3.a. The three devices exhibiting similar maximum values of g_m/W also have a similar L_c , while the longer channel devices have longer contacts. Finally, the device with $L = 60 \text{ nm}$ and $L_c = 140 \text{ nm}$ exhibits the lowest $g_m/W = 3 \text{ S m}^{-1}$.

The contact resistance of OTFTs with a staggered geometry is usually described by the current crowding model,²³ according to which the current is not uniform along the length of the contact and the largest proportion of charges is injected at the contact edge near the channel. The characteristic transfer length over which most of the charges are injected is $L_T = \sqrt{r_c/r_{ch}}$, where r_c is the interfacial contact resistivity (in $\Omega \text{ cm}^2$) and $r_{ch} = [\mu C_i(V_G - V_T)]^{-1}$ is the channel sheet resistance. The model yields a contact resistance $R_c W = L_T r_{ch} \coth(L_c/L_T)$. However, if the contact length is reduced below the transfer length, to a first order approximation $\coth(L_c/L_T) = L_T/L_c$ and the contact resistance becomes $R_c W = r_c/L_c$. The total resistance of the device in Figure 2c at $V_G = -0.7 \text{ V}$ is only $R_t W = 15 \Omega \text{ cm}$, much lower than the aforementioned value for the microscale device of Figure 1c and approaching the previously reported contact resistance of ion gel-gated OECTs.²⁰ It is therefore reasonable to assume that $R_t \simeq R_c$ and $R_t W$ should scale as L_c^{-1} . Because of the limited resolution of the single-layer resist lift-off process used here to pattern the contacts, there is a significant spread of the data at small L_c , but Figure 3.b shows that this trend is observed for P3HT nanoscale ion gel-gated OECTs, indicating that the magnitude of the on-current is indeed limited by contact resistance. The conductivity of the ion-doped channel is so high that when a current flows, despite the efficient injection process, the source contact cannot supply enough carriers per unit time and the entire contact is involved in the process ($L_c < L_T$). Nonetheless, g_m/W increased by a factor of nearly 20 between the devices shown in Figure 1 and Figure 2, attesting to the value of reducing the device footprint. Moreover, confronted with the evidence that the total device resistance is

largely dominated by the contact resistance, it is all the more astounding that I_D evolves linearly with V_D at small biases.

Overall, the static performance of the nanoscale ion gel-gated OECTs reported here compares very favourably to that of state-of-the-art nanoscale OTFTs prepared using a high mobility polycrystalline small molecule semiconductor deposited by sublimation in vacuum and a bilayer insulator comprised of an ultrathin AlO_x layer and a SAM, as well as a selective contact-doping method¹ (Table 1). They also vastly outperform nanoscale polyelectrolyte-gated EDL transistors. The fabrication process of nanoscale ion gel-gated OECTs necessitates no high processing temperatures or vacuum, apart from the metal contacts, which can be replaced by solution-processable materials such as PEDOT:PSS, carbon nanotubes, metal nanowires or graphene.²⁴ This opens the possibility of high-performance nanoscale devices prepared using high-resolution and low-cost solution processing methods such as photolithography,²¹ inkjet printing,²⁵ nanoimprint lithography^{26,27} or soft lithography.²⁸

Table 1: Comparison of nanoscale OTFT technologies

	W (μm)	L (nm)	L_c (nm)	V_G (V)	I_D (μA)	on-to-off ratio	g_m/W (S m^{-1})	$R_t W$ ($\Omega \text{ cm}$)
Ref. 12 ^a	500	200	–	–1	–25	25	0.15	–
Ref. 1 ^b	0.5	150	200	–3	–0.09	10^7	0.4	2.7×10^3
This work ^c	100	50	550	–1	–650	10^8	12	15

^a Insulator: polyelectrolyte (55 nm), semiconductor: P3HT; ^b Insulator: AlO_x (3.6 nm) & SAM (2.1 nm), semiconductor: polycrystalline small molecule; ^c Insulator: ion gel ($> 10 \mu\text{m}$), semiconductor: P3HT.

Conventionally, shortening the transistor channel is also associated with faster operation, since the time needed to switch the device on ideally scales as L^2 , if it is only limited by the hole transit time across the channel.^{3,12} For ion-gated OTFTs, however, it was shown that below a threshold L , the dynamic performance of the device is instead restrained by ionic motion.^{12,29} Concerning ion gel-gated OECTs, Frisbie et al. identified the parasitic overlap capacitance between the ion gel and the contacts as a possible limiting factor and were able to reach an operating frequency $f = 10 \text{ kHz}$ by reducing the overlap area, $W \times L_c$, in their aerosol-jet-printed devices.³⁰ The switching time of the nanoscale P3HT devices was evaluated by applying a square wave pulse to the gate and measuring the resulting drain current (Supporting Figure S1). The devices could be switched both on and off in

about 20 ms (calculated by including 90 % of the response), or an equivalent operating frequency $f = 50$ Hz, which is not only relatively slow, but it is the same value as the one we reported earlier for long-channel ion gel-gated OECTs with the same semiconductor layer thickness.²¹ The slow switching of P3HT devices and the invariance of the switching time with L and $W \times L_c$ indicates that neither the hole transit time or the parasitic overlap capacitance are responsible for the observed response times. Instead, ion migration in and out of the semiconductor likely dominates and is not optimal in this polymer when prepared with the process used here. State-of-the-art performance is not the aim of this study, but our devices clearly underperformed compared to what the Frisbie group reported using the same semiconductor and anion. This result strongly suggests that there must be other factors hindering ionic motion that are associated with the polymer film microstructure, such as its density, porosity and crystalline fraction, which are heavily influenced by the fabrication process used. Further investigation is really needed to identify the links between microstructure and ion transport.

Figure 4: Short-channel p(g2T-TT) device. (a) Chemical structure of the polymer semiconductor p(g2T-TT). (b) Output and (c) transfer characteristics and width-normalized transconductance of a p(g2T-TT) device with $L = 60$ nm and $L_c = 550$ nm.

To confirm that reducing the device dimensions can lead to a significant increase in operating frequency when ion migration in and out of the semiconductor is not the sole limiting factor, nanoscale ion gel-gated OEETs were prepared using a different polymer, p(g2T-TT) (Figure 4a), which was recently shown to be a good anion conductor when gated with an aqueous electrolyte, thanks to its polar glycol side-chains.³¹ We use it here for the first time with a non-aqueous electrolyte, in an attempt to show that it is more efficient than P3HT at transporting the unsolvated TFSI⁻ molecular anions (see Supporting Figure S2 for the characteristics of microscale devices). The static electrical characteristics of p(g2T-TT) nanoscale ion gel-gated OEETs once again afforded a very high g_m/W and a two order of magnitude increase in on-to-off ratio relative to the microscale devices. Even though R_tW was likewise observed to scale linearly with L_c^{-1} (Figure 3b), the output curves once more afforded a linear evolution of the drain current at low drain voltages and clear saturation at higher voltages, as shown in Figure 4b–c. Hence, the conclusions reached for P3HT seem to be universal and not material-specific, and should be generalizable to other conjugated polymers in the future. The major differences compared to the P3HT characteristics are the more positive turn-on voltage, which we attribute to a smaller ionisation potential, and a steeper subthreshold slope, which suggests more efficient ionic transport. However, the off-current is about one order of magnitude higher than in the P3HT devices and the hysteresis in the on-state is higher. The origin of these observations is unknown at this time and will require further studies.

Transient measurements made on long-channel ($L_c = 5\text{ }\mu\text{m}$, $L = 10\text{ }\mu\text{m}$) ion gel-gated OEETs based on this semiconductor revealed it could be switched on in about 3 ms, i.e. $f = 300\text{ Hz}$, six times faster than P3HT devices (Supporting Figure S3a), confirming the superior ionic transport capabilities of p(g2T-TT). More interestingly, nanoscale ion gel-gated OEETs could be switched on in about 300 μs and off in 200 μs , as shown in Supporting Figure S3b for a device with $L = 60\text{ nm}$ and $L_c = 500\text{ nm}$, that is $f = 3\text{ kHz}$. This suggests that, if ionic transport in the semiconductor can be improved so as not to be the

factor limiting the device switching speed (as seems to be the case for the P3HT devices fabricated using our process), the parasitic overlap capacitance can play an important role in limiting the device speed and reducing the device dimensions can lead to a significant increase in operating frequency. However, all the nanoscale p(g2T-TT) tested in this work, which had L ranging from 1000 to 60 nm and L_c ranging from 1000 to 150 nm, exhibited similar switching times, suggesting that, at these dimensions, ion migration in and out of the semiconductor once again takes over as the main factor limiting the device speed. Combining nanoscale device dimensions, in order to limit the overlap capacitance, with a fabrication process optimized to result in a polymer microstructure that favours ion transport, could potentially yield significant improvements in device speed in the future.

In addition to being an important finding from a theoretical perspective, the absence of short-channel effects in nanoscale ion gel-gated OECTs has significant implications for potential practical applications. While very fast switching speeds is generally the primary reason for shortening the channel of conventional OTFTs, ion gel-gated OECTs do not exceed operating frequencies of the order of 10 kHz for the aforementioned reasons. However, ion gel-gated OECTs are particularly suited for solid-state sensors and sensor arrays, where the operating frequency is not as critical and is balanced with other parameters such as cost, flexibility, transparency, resolution or transconductance. They are envisioned for use in wearable electronics for health monitoring,³² in vivo brain interfacing^{33,34} or electronic skins.³⁵ An active matrix sensor array is composed of a grid of pixels, with each pixel comprising a sensor, such as a pressure or temperature-sensitive component^{36–39} or a biofunctionalized electrode,⁴⁰ and a readout transistor that is selectively turned on when the state of a particular pixel is read. In order to avoid the need for additional post-processing in a complex external circuit and reduce interference, an additional transistor can be included to the sensor circuitry to intrinsically amplify the signal at the pixel level.³⁵ The sensor can be connected to the (floating) gate electrode or directly incorporated as the gate dielectric of the transistor. This transistor should have a high transconductance in order to maximize

the signal-to-noise ratio of the sensor.³⁴

Arrays consisting of depletion-mode PEDOT:PSS electrochemical transistor sensors connected to conventional organic field-effect readout transistors have been demonstrated,⁴¹ but using both types of devices considerably increased the complexity of the fabrication process and the pixel footprint. The advantage of using solid-state nanoscale ion gel-gated OECTs is that the same materials and architecture can be used for both the readout and sensor/amplifier transistors, thanks to their low off-currents and high transconductance. The very small footprint of nanoscale ion gel-gated OECTs also gives the ability to either increase the area of the sensing elements relative to the total size of each pixel, which in turn increases the signal-to-noise ratio, or to reduce the overall size of the pixels to achieve very high spatial resolutions. In addition, in applications where a very high gain is desired, a P3HT ion gel-gated OECT with $L = 50$ nm, $L_c = 550$ nm and interdigitated contacts such that the device footprint is $100 \times 100 \mu\text{m}^2$ would for example exhibit a very large transconductance of about 100 mS, more than 300 times that of a device with $L = 10 \mu\text{m}$, $L_c = 5 \mu\text{m}$ and the same footprint.

In conclusion, we have shown that ion gel-gated OECTs do not seem to suffer from the same short-channel limitations as OTFTs operated in the field-effect mode, down to a channel length of 50 nm. Nanoscale ion gel-gated OECTs conserve the excellent properties of their larger counterparts, such as ultralow operating voltages ($\leq |1 \text{ V}|$), large on-currents and saturating output curves, and even exhibit improvements in their electrical characteristics such as a record-high width-normalized transconductance for solid-state OTFTs and an increase of two orders of magnitude in the on-to-off ratio, arising from a dramatic reduction in the off-current. Despite evidence that the contact resistance dominates the total device resistance, the output curves show no signs of nonlinearities at small drain voltages. Using a polymer semiconductor with a good ionic conductivity, miniaturisation also yields much faster devices. The outstanding performance of nanoscale ion gel-gated OECTs makes them excellent candidates for the fabrication of high-gain solid-state sensors and sensor arrays

using inexpensive and unsophisticated patterning methods.

Acknowledgement

This work was supported by the European Commission's 7th Framework Programme (FP7/2007-2013) under grant agreement no. 607896 (OrgBIO). We also thank J. Cambiasso for helpful discussions on electron-beam lithography and for helping with SEM imaging.

Supporting Information Available

Experimental methods, transient response of a P3HT nanoscale device, electrical characteristics of a microscale p(g2T-TT) device and transient responses of p(g2T-TT) macroscale and nanoscale devices.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References

- (1) Ante, F.; Kälblein, D.; Zschieschang, U.; Canzler, T. W.; Werner, A.; Takimiya, K.; Ikeda, M.; Sekitani, T.; Someya, T.; Klauk, H. *Small* **2011**, *7*, 1186–1191.
- (2) Ante, F.; Kälblein, D.; Zaki, T.; Zschieschang, U.; Takimiya, K.; Ikeda, M.; Sekitani, T.; Someya, T.; Burghartz, J. N.; Kern, K. et al. *Small* **2012**, *8*, 73–79.
- (3) Haddock, J. N.; Zhang, X.; Zheng, S.; Zhang, Q.; Marder, S. R.; Kippelen, B. *Org. Electron.* **2006**, *7*, 45–54.
- (4) Li, J.; Zhao, Y.; Tan, H. S.; Guo, Y.; Di, C.-A.; Yu, G.; Liu, Y.; Lin, M.; Lim, S. H.; Zhou, Y. et al. *Sci. Rep.* **2012**, *2*, 754.
- (5) Diao, Y.; Tee, B. C.; Giri, G.; Xu, J.; Kim, D. H.; Becerril, H. A.; Stoltenberg, R. M.; Lee, T. H.; Xue, G.; Mannsfeld, S. C. B. et al. *Nat. Mater.* **2013**, *12*, 665–671.

- (6) Venkateshvaran, D.; Nikolka, M.; Sadhanala, A.; Lemaire, V.; Zelazny, M.; Kepa, M.; Hurhangee, M.; Kronemeijer, A. J.; Pecunia, V.; Nasrallah, I. et al. *Nature* **2014**, *515*, 384–388.
- (7) Niazi, M. R.; Li, R.; Qiang Li, E.; Kirmani, A. R.; Abdelsamie, M.; Wang, Q.; Pan, W.; Payne, M. M.; Anthony, J. E.; Smilgies, D.-M. et al. *Nat. Commun.* **2015**, *6*, 8598.
- (8) Tulevski, G. S.; Nuckolls, C.; Afzali, A.; Graham, T. O.; Kagan, C. R. *Appl. Phys. Lett.* **2006**, *89*, 183101.
- (9) Collet, J.; Tharaud, O.; Chapoton, A.; Vuillaume, D. *Appl. Phys. Lett.* **2000**, *76*, 1941–1943.
- (10) Fujimori, F.; Shigeto, K.; Hamano, T.; Minari, T.; Miyadera, T.; Tsukagoshi, K.; Aoyagi, Y. *Appl. Phys. Lett.* **2007**, *90*, 193507.
- (11) Herlogsson, L.; Crispin, X.; Robinson, N. D.; Sandberg, M.; Hagel, O. J.; Gustafsson, G.; Berggren, M. *Adv. Mater.* **2007**, *19*, 97–101.
- (12) Herlogsson, L.; Noh, Y.-Y.; Zhao, N.; Crispin, X.; Sirringhaus, H.; Berggren, M. *Adv. Mater.* **2008**, *20*, 4708–4713.
- (13) Thiburce, Q.; Campbell, A. J. *Adv. Electron. Mater.* **2017**, *3*, 1600421.
- (14) Cho, J. H.; Lee, J.; Xia, Y.; Kim, B.; He, Y.; Renn, M. J.; Lodge, T. P.; Daniel Frisbie, C. *Nat. Mater.* **2008**, *7*, 900–906.
- (15) Hong, K.; Kim, Y. H.; Kim, S. H.; Xie, W.; Xu, W. D.; Kim, C. H.; Frisbie, C. D. *Adv. Mater.* **2014**, *26*, 7032–7037.
- (16) Lee, J.; Kaake, L. G.; Cho, H. J.; Zhu, X. Y.; Lodge, T. P.; Frisbie, C. D. *J. Phys. Chem. C* **2009**, *113*, 8972–8981.

- (17) Rivnay, J.; Leleux, P.; Ferro, M.; Sessolo, M.; Williamson, A.; Koutsouras, D. A.; Khodagholy, D.; Ramuz, M.; Strakosas, X.; Owens, R. M. et al. *Sci. Adv.* **2015**, *1*, e1400251–e1400251.
- (18) Khodagholy, D.; Rivnay, J.; Sessolo, M.; Gurfinkel, M.; Leleux, P.; Jimison, L. H.; Stavrinidou, E.; Herve, T.; Sanaur, S.; Owens, R. M. et al. *Nat. Commun.* **2013**, *4*, 2133.
- (19) Inal, S.; Malliaras, G. G.; Rivnay, J. *Nat. Commun.* **2017**, *8*, 1767.
- (20) Braga, D.; Ha, M.; Xie, W.; Frisbie, C. D. *Appl. Phys. Lett.* **2010**, *97*, 193311.
- (21) Thiburce, Q.; Porcarelli, L.; Mecerreyes, D.; Campbell, A. J. *Appl. Phys. Lett.* **2017**, *110*, 233302.
- (22) Donahue, M. J.; Williamson, A.; Strakosas, X.; Friedlein, J. T.; McLeod, R. R.; Gleskova, H.; Malliaras, G. G. *Adv. Mater.* **2018**, *30*, 1705031.
- (23) Richards, T. J.; Sirringhaus, H. *J. Appl. Phys.* **2007**, *102*, 094510.
- (24) Hecht, D. S.; Hu, L.; Irvin, G. *Adv. Mater.* **2011**, *23*, 1482–1513.
- (25) Noh, Y.-Y.; Zhao, N.; Caironi, M.; Sirringhaus, H. *Nat. Nanotechnol.* **2007**, *2*, 784–789.
- (26) Higgins, S. G.; Muir, B. V. O.; Wade, J.; Chen, J.; Striedinger, B.; Gold, H.; Stadlober, B.; Caironi, M.; Kim, J.-S.; Steinke, J. H. G. et al. *Adv. Electron. Mater.* **2015**, *1*, 1500024.
- (27) Austin, M. D.; Chou, S. Y. *Appl. Phys. Lett.* **2002**, *81*, 4431–4433.
- (28) Wang, Z.; Xing, R.; Yu, X.; Han, Y. *Nanoscale* **2011**, *3*, 2663.
- (29) Xia, Y.; Zhang, W.; Ha, M.; Cho, J. H.; Renn, M. J.; Kim, C. H.; Frisbie, C. D. *Adv. Funct. Mater.* **2010**, *20*, 587–594.

- (30) Zare Bidoky, F.; Frisbie, C. D. *ACS Appl. Mater. Interfaces* **2016**, *8*, 27012–27017.
- (31) Giovannitti, A.; Sbircea, D.-T.; Inal, S.; Nielsen, C. B.; Bandiello, E.; Hanifi, D. A.; Sessolo, M.; Malliaras, G. G.; McCulloch, I.; Rivnay, J. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 12017–12022.
- (32) Kenry,; Yeo, J. C.; Lim, C. T. *Microsyst. Nanoeng.* **2016**, *2*, 16043.
- (33) Viventi, J.; Kim, D.-H.; Vigeland, L.; Frechette, E. S.; Blanco, J. A.; Kim, Y.-S.; Avrin, A. E.; Tiruvadi, V. R.; Hwang, S.-W.; Vanleer, A. C. et al. *Nat. Neurosci.* **2011**, *14*, 1599–1605.
- (34) Khodagholy, D.; Doublet, T.; Quilichini, P.; Gurfinkel, M.; Leleux, P.; Ghestem, A.; Ismailova, E.; Hervé, T.; Sanaur, S.; Bernard, C. et al. *Nat. Commun.* **2013**, *4*, 1575.
- (35) Chortos, A.; Liu, J.; Bao, Z. *Nat. Mater.* **2016**, *15*, 937–950.
- (36) Someya, T.; Kato, Y.; Sekitani, T.; Iba, S.; Noguchi, Y.; Murase, Y.; Kawaguchi, H.; Sakurai, T. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 12321–12325.
- (37) Sekitani, T.; Zschieschang, U.; Klauk, H.; Someya, T. *Nat. Mater.* **2010**, *9*, 1015–1022.
- (38) Takei, K.; Takahashi, T.; Ho, J. C.; Ko, H.; Gillies, A. G.; Leu, P. W.; Fearing, R. S.; Javey, A. *Nat. Mater.* **2010**, *9*, 821–826.
- (39) Kaltenbrunner, M.; Sekitani, T.; Reeder, J.; Yokota, T.; Kuribara, K.; Tokuhara, T.; Drack, M.; Schwödiauer, R.; Graz, I.; Bauer-Gogonea, S. et al. *Nature* **2013**, *499*, 458–463.
- (40) White, S. P.; Dorfman, K. D.; Frisbie, C. D. *Anal. Chem.* **2015**, *87*, 1861–1866.
- (41) Lee, W.; Kim, D.; Matsuhisa, N.; Nagase, M.; Sekino, M.; Malliaras, G. G.; Yokota, T.; Someya, T. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 201703886.

Graphical TOC Entry