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DNA detection with a water-gated organic field-effect transistor

Loig Kergoat [a,b], Benoît Piro [a], Magnus Berggren [b], Minh-Chau Pham [a,*], Abderrahim Yassar [c], Gilles Horowitz [a,c]

[a] Laboratoire Interfaces-Traitements-Organisation et Dynamique des Systèmes (ITODYS), Associé au CNRS-UMR 7086, Université Paris Diderot – Sorbonne Paris Cité, 15 Rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France
[b] Organic Electronics, Dept. of Sciences and Technology (ITN), Linköpings Universitet, Bredgatan 33, SE-601 74 Norrköping, Sweden
[c] Laboratoire des Interfaces et des Couches Minces (LPICM), CNRS-UMR 7647, Ecole Polytechnique, 91128 Palaiseau, France

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ABSTRACT

A DNA sensor based on a water-gated organic field-effect transistor is described. The semiconductor is poly [3-(5-carboxypentyl)thiophene-2,5-diyl] onto which DNA probes are covalently grafted via NHS/EDC chemistry. Clear changes in the output characteristic of the device are observed upon DNA immobilization and after DNA hybridization. Experimental data point out the importance of the electrolyte Debye length that can screen negative DNA charges and impede transduction. For this reason, deionized water was used in order to increase the Debye length up to several hundreds of nanometers. In this case, a decrease in the off current was observed upon hybridization, whereas no significant change occurred when using saline solutions.

1. Introduction

A current challenge in DNA detection is to develop fast, low-cost, simple and sensitive methods. As hybridization does not imply electronic transfer or results in any product, the detection scheme usually relies on the change in structure upon hybridization or, most often, on the use of a label attached to the target sequence. The transduction can be measured optically [1,2] or using mass-sensitive devices [3,4].

The electrochemical methods are studied more recently and can be sorted in two categories: direct or indirect, depending on whether they are label-free [5,6] or use labelled targets [7,8]. Particularly, organic electrochemical transistors give interesting results [9,10].

Because DNA can be considered as a polyelectrolyte (each phosphate group carries a negative charge at neutral pH), field-effect-based transistors, which are very sensitive to changes in surface potential, are potential transducers for DNA detection. Furthermore, the inherent miniaturization of these devices and their compatibility with advanced micro-fabrication technology make them very attractive for DNA microarrays. In 1970, Bergveld first described the use of field-effect transistors as sensing devices, developing the so-called ion-sensitive field-effect transistor (ISFET) [11]. While for the metal–oxide-semiconductor field effect transistor (MOSFET) the threshold voltage at which the transistor switches on only depends on the nature of the metal and the semiconductor, the threshold voltage of the ISFET is sensitive to the interfacial potential at the electrolyte/insulator interface. Hence, any change in this interfacial potential, such as the presence of charged molecules (e.g. DNA), would result in a shift in the conductance of the semiconductor [12–14]. Original architectures emerged later, such as charge-modulated FET (CM-FET) [15], or devices based on nanotubes and nanodiamonds [16,17]. Recently, DNA sensors based on graphene were also reported [18]. However, organic semiconductors constitute an excellent alternative to inorganic semiconductors, allowing mass-production at

* Corresponding author. Tel.: +33 1 57277223.
E-mail address: mcpham@univ-paris-diderot.fr (M.-C. Pham).

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low cost [19]. Still, few works were reported on organic FET configuration (OFETs). A pentacene-based OFET sensitive to DNA adsorption was described by Zhang et al. and Stoliar et al. [20,21]. Roberts et al. [22,23] developed a general approach for sensing in aqueous media, based on the incorporation of an ultrathin dielectric layer on top of the semiconductor. This reduces the operating voltage thus minimizes the parasitic ionic current that typically plagues OFET operating in water.

Electrolytic gate FETs (EGOFETs) have attracted attention lately due to their low-voltage operation compared to conventional insulators. In this case, the high electric field generated at the interface results in higher charge density, thus generating higher mobility and higher output currents [24–26]. Polymer semiconductors gated via a polymer electrolyte were also studied [27]. Compared to solid dielectrics, the main issue with electrolytes is slower switching time, usually limited to 100 Hz. To improve the device speed, it was proposed to reduce the channel size [28]. Another approach is the use of ion-gels, formed by gelation of a block copolymer in an ionic liquid [29].

One more serious issue with those devices is that electrochemical switching and field-effect modulation often coexist [30,31] resulting in large hysteresis. We recently attempted to replace the gate dielectric by a simple water droplet and reported an OFET gated via pure water (WGOFET) that operates entirely in the field-effect mode. The main advantages of these water-gated devices reside in their very easy fabrication and very low operation voltage (below 1 V), opening up to applications in biosensing in aqueous media [32].

In this work, we present applications of WGOFET to DNA detection. As discussed above, DNA as charged molecules are well adapted for application in EGOFETs. However, using conventional electrolytes could induce screening of DNA charges due to the rather high ionic concentration in the solution. In WGOFETs, deionized water can be used instead of more concentrated electrolytes. For this reason, the water-gated transistor appears very pertinent for DNA detection.

2. Experimental

2.1. Chemicals

Poly(3-hexylthiophene) (P3HT) (MW = 37000 g mol^{-1}, 98% regioregular) and poly [3-(5-carboxypentyl)thiophene-2,5-diyl] (P3PT–COOH) were purchased from Sigma–Aldrich and Rieke Metals Inc., respectively, and used without further purification (see Fig. S1, Supporting Information). P3PT–COOH meets the requirements: good chemical stability, high charge mobility and a carboxylic group available for grafting DNA. Due to the presence of carboxylic acid moieties, the solubility of this material is very low in most solvents. Nevertheless, a good solubility was obtained in dimethylformamide (DMF).

Solutions of P3HT and P3PT–COOH (8 mg mL^{-1}) were prepared by dissolving in chlorobenzene and DMF, respectively, under stirring and heating up to 60 °C. The solutions were filtered with 200 nm PTFE filter. OFET were realized by spin-coating these solutions on photolithography-patterned gold contacts.

Ultra-pure H_2O (18 MΩ cm) was obtained from Elgastat UHQ II purification system.

DNA sequences come from the HIV virus. The probe contains the GEM sequence, which is complementary to the Gag gene, one of the three main HIV genes. A non-complementary sequence (randomly distributed bases, RAND) was also used. The nature and properties of the ODN strands are described in Table 1.

Table 1
Name, function, sequence and melting temperature of the studied ODN.

Name	Function	Sequence	T_m/°C
GEM	Probe	5′-TC-GC-ACC-CAT-CTC-TCT-CCT-TCT-AGCCT-3′-C_6NH_2	
HIV	Compl. target	3′-CG-TGG-GTA-GAG-AGA-GGA-AGA-5′	62
RAND	Random target	3′-CG-TAA-ATG-ATC-CTT-CAA-CTA-5′	No hyb.

2.2. Device

A general view of the device is sketched in Fig. 1. The transistors were built in bottom contact, top gate configuration. The substrate consisted of a silicon wafer with 300 nm thermally grown oxide. Contacts were made of gold (50 nm) evaporated on a thin titanium attachment layer (5 nm) then patterned by photo-lithography.

P3HT or P3PT–COOH solutions were spin-coated onto the substrates at 1500 rpm for 30 s in ambient conditions. The devices were then kept overnight in oven at 110 °C under 50 mbar pressure to remove the residual solvent. A water droplet was deposited onto the semiconductor before use. The gate electrode consisted of a platinum wire dipped into the droplet.

2.3. Procedures

In a first step, probe ODN are immobilized onto the P3PT–COOH. Samples are placed in an aqueous solution containing 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, $C = 2 \times 10^{-2}$ mol L^{-1}), *N*-hydroxysuccinimide (NHS, $C = 2 \times 10^{-2}$ mol L^{-1}) and the probe ODN (C = 1 μmol L^{-1}) and kept overnight in a thermostatic bath at 37 °C.

After ODN immobilization, transistors are washed for 2 h in PBS solution at 37 °C in order to get rid of the residual non grafted ODNs. Then they are dipped in the hybridization solution, i.e. a PBS solution containing the ODN

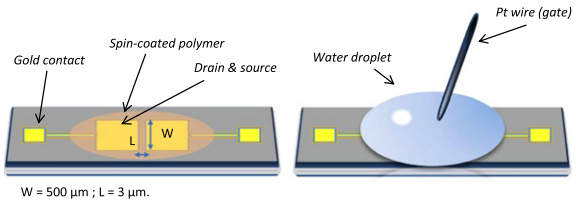

Fig. 1. Schematic view of the OFET device.

target at various concentrations, from 1 nM to 100 nM; results showed that concentrations lower than 100 nM give too weak changes in the transfer characteristics. The solution is heated up to 70 °C (higher than the melting temperature of the complementary sequence) for 2 h, then slowly cooled down to 37 °C to make efficient hybridization. Finally, the samples are washed for one additional hour in PBS solution at 37 °C to eliminate non hybridized ODN strands.

The use of fluorophore-modified targets is useful to validate the immobilization method as well as to quantify the number of probes grafted onto the surface. Target strands are modified on their 3′-end with fluorescein (excitation and emission wavelengths at 492 nm and 525 nm, respectively). A four-step washing procedure is realized in mild conditions, the first three steps in PBS at 37 °C for 10, 12 and 15 min to remove ODN strands adsorbed on the surface. For one experiment, pure water was used instead of PBS. Finally, in the fourth step, the denaturation is carried out by dipping the samples in pure water and heating up above 90 °C, these rough conditions ensuring a full dissociation of the double strands. The solutions of each step are collected and analyzed by fluorescence spectroscopy.

3. Results and discussions

3.1. Electrical characterizations

3.1.1. P3HT in deionized H_2O

The device was first evaluated with P3HT (Fig. 2a) for drain voltages between 0 V and −0.6 V and gate voltages between +0.5 V and −0.5 V. Selected curves at a drain voltage of −0.5 V are shown in Fig. 2b. The curves show relatively low hysteresis, in agreement with what usually observed with P3HT.

3.1.2. P3PT–COOH in deionized H_2O

The device was then evaluated with P3PT–COOH under the same experimental conditions than with P3HT (Fig. 2c and d). A significant hysteresis is observed on both curves, which can be attributed to several factors. First, ion

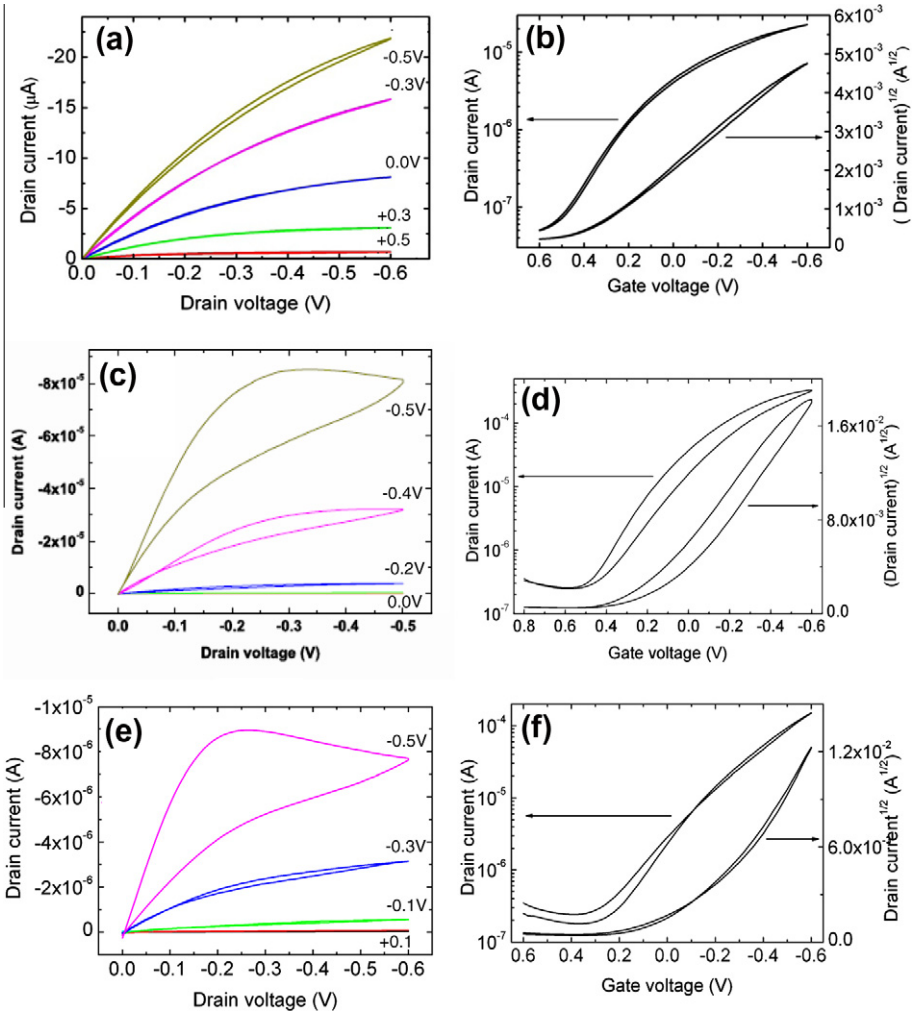

Fig. 2. I–V characteristics for P3HT: (a) output and (b) transfer curves; for P3PT–COOH in water: (c) output and (d) transfer curves; for P3PT–COOH in PBS: (e) output and (f) transfer curves. Transfer curves obtained at $V_d = -0.5$ V.

penetration in the bulk of the semiconductor is more likely to occur than with P3HT (the contact angle of P3PT–COOH was around 50° against 95° for P3HT). This less hydrophobic character may favor ion penetration into the polymer. An alternative explanation is the slow formation of the electrical double layer because of the low ionic concentration of deionized water.

3.1.3. P3PT–COOH in PBS

The electrical characteristics obtained with PBS instead of water are shown in Fig. 2e and f. The hysteresis is less pronounced than in the case of pure water (f to be compared to d). This confirms that higher ionic concentration leads to faster polarization time due to a faster electrical double layer formation. Nonetheless, the rather high hysteresis compared to P3HT indicates that ion penetration still occurs. This behavior slightly degrades the device stability upon cycling of the gate voltage. However, three transfer curves can be recorded consecutively without noticeable change of the shape.

3.2. DNA detection

3.2.1. DNA probe grafting

We first studied the effect of immobilizing an ODN probe onto the semiconductor surface. Fig. 3 compares the transfer characteristics of a device modified with ODNs (Fig. 3a) to that of a device prepared under the same conditions but without ODNs (Fig. 3b). The transfer curves were recorded on the bare film before and after ODN immobilization. After ODN immobilization, we observe a clear drop of the *off* current and maximum drain current, along with a shift towards negative voltages. Conversely, the *off* current increases and shifts towards positive voltages for devices without ODNs.

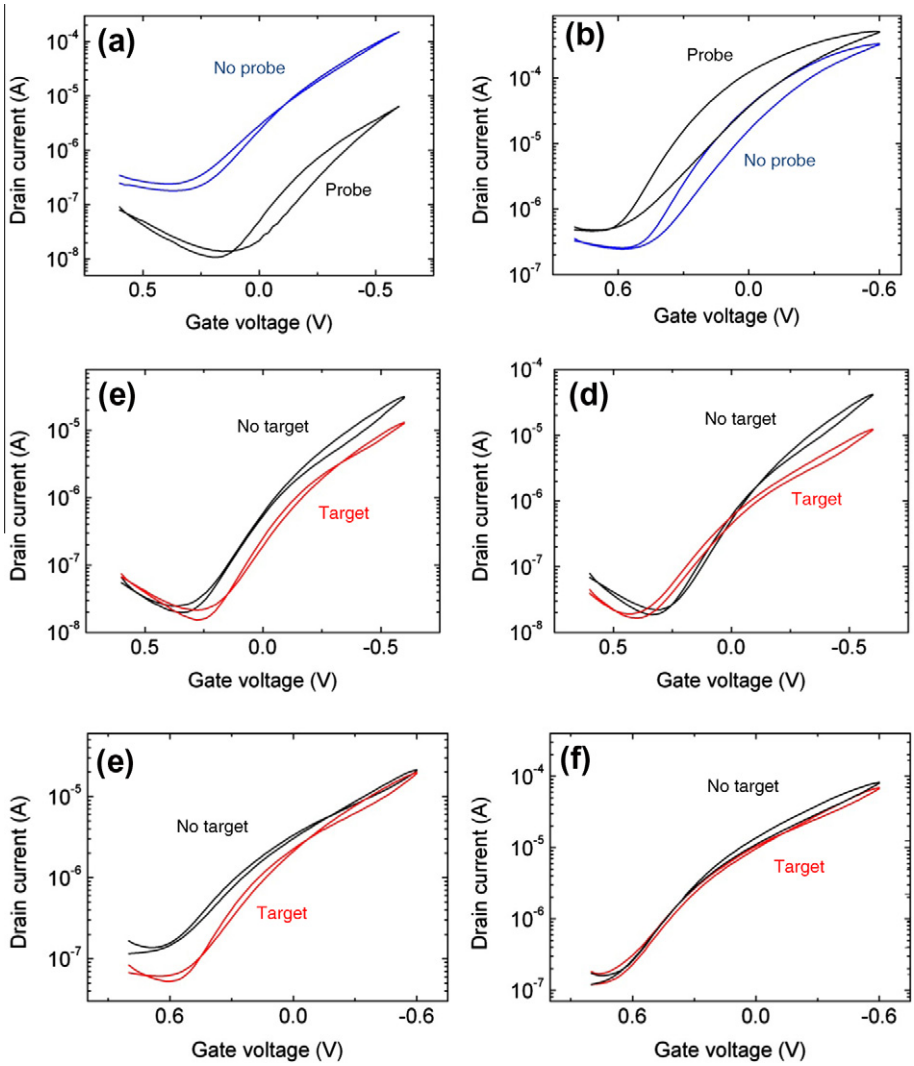

Fig. 3. Modification of the transfer characteristics after (a) immobilization of ODNs and (b) a blank sample after soaking in a bath similar to (a) but without ODNs; Transfer curves for hybridization with (c) a complementary target and (d) a random target; Transfer curves for (e) a complementary target and (f) a random target in pure water instead of PBS.

Table 2
Debye length as a function of PBS dilution.

PBS dilution	1	0.1	0.05	0.02	0.01	Carbonated H_2O (18 MΩ)
λ_D/nm	0.76	2.41	3.40	5.38	7.61	206

Because of the electrochemical doping, neither mobility nor the threshold voltage are pertinent parameter. Instead, we chose as criteria the V_{Gmin} position and the minimum intensity of the drain current (Table 3). Field-effect transistors are very sensitive to the presence of charges at the semiconductor–insulator interface, which leads to a shift of the onset voltage. For a p-channel OFET, the negative surface charges brought by the ODN backbone must be compensated by positive holes injected into the channel before any substantial current can flow between source and drain. This results in a shift of the transfer curve towards negative gate voltages. We note that a similar behavior has been reported on similar devices based on graphene sheets [18]. Conversely, when no ODN is grafted, V_{Gmin} moves towards positive voltages. Because of the carboxylate moieties present on the polymer backbone, it is likely that upon applying a positive bias to the gate, cations from the solution penetrate into the semiconductor bulk. As a consequence, the concentration of positive charges at the electrolyte/semiconductor interface is higher and fewer holes have to be injected to switch the transistor on, so that even the off current increases. By contrast, the presence of ODN strands on top of the semiconductor seems to prevent or at least decrease ion penetration into the polymer bulk [6], as indicated by the drop of the off current. This shielding by DNA strands makes sense if we consider that even if the surface concentration of ODN is low, the surface that is actually covered by ODN is high (a 20 bases-long ODN has a gyration radius of several nm), so that it seems reasonable to suppose that immobilized DNA strands (single strands), which are polyelectrolytes, act as an electrostatic barrier that prevents (or at least impede) ion diffusion through the interface.

3.2.2. Target detection

Hybridization, which results in conformational changes (formation of rigid double helix) should modify the interface properties, then modify the transfer characteristics (Fig. 3c and d). A significant shift of the V_{gmin} towards negative voltages is seen for complementary strands, and towards positive voltages in the case of random targets (Table 3). Changes are relatively weak under these experimental conditions. A well-known issue with charge-sensitive devices such as FETs is the electrical screening effect due to the rather high ionic concentration in biological fluids like PBS. A key parameter is the Debye length. In electrolytes, charged molecules are screened by dissolved counterions and in our case, DNA could be surrounded by positively charged ions due to electrostatic interactions. Over a given length scale, the so-called Debye length, the number of net positive charges approaches that of negative charges on DNA backbone. This results in a screening effect so that the electrostatic potential arising from charges on DNA exponentially decays towards zero with distance.

Eq. (1) gives the Debye length for an aqueous solution, at room temperature. $\varepsilon_d = \varepsilon_r\ \varepsilon_0$, where ε_0 is the dielectric permittivity of vacuum (8.85×10^{-12} F m^{-1}), and $\varepsilon_r = 80$, the relative permittivity of water at room temperature. k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}), T the absolute temperature, q_i the charge carried by the ionic species i and c_i^0 its ionic concentration, expressed in m^{-3}, that should be multiplied by $10^3 \times N_a$ (6.022×10^{23}) to use mol dm^{-3} unit.

$$\lambda_D = \sqrt{\frac{\varepsilon_d k_B T}{\sum_i q_i^2 C_i^0}} \quad (1)$$

Using Eq. (1) along with the ionic concentrations in PBS (Table S2, Supporting Information) leads to the data of Fig. S3; values of λ_D are given in Table 2.

If we consider that an ODN sequence composed of 27 bases has a length of approximately 9 nm when included in a double strand, most of the negative charges lie outside the screening distance in PBS, because the respective Debye length is $\lambda_D = 0.76$ nm (cf. Fig. S4a). In order to address this issue, we changed the PBS solution to 18 MΩ DI water ($\lambda_D = 206$ nm, cf. Fig. S4b). The corresponding I–V curves are shown in Fig. 3e and f.

Using DI water instead of PBS modifies the response of our devices upon hybridization. A decrease of the *off*-current is observed for the complementary strands whereas there is no significant change with the random target (Data are

Table 3
Influence of grafting and hybridization on device performance with PBS as electrolyte, and influence of hybridization with water as electrolyte.

ODN grafting (Fig. 3a and b)			
ODN probe	ΔV_{Gmin}/V	$I_{off\ (bare\ film)}/I_{off\ (probe\text{-}modified\ film)}$	Number of transistors
Yes	−0.31 ± 0.05	11.1 ± 3.7	15
No	+0.16 ± 0.05	0.5 ± 0.12	9
DNA hybrid. in PBS (Fig. 3c and d)			
ODN target	ΔV_{Gmin}/V	$I_{off\ (probe\text{-}modified\ film)}/I_{off\ (hybridization)}$	Number of transistors
HIV	−0.06 ± 0.02	1.7 ± 0.45	15
RAND	−0.03 ± 0.03	1.3 ± 0.28	15
DNA hybrid. in H_2O (Fig. 3e and f)			
ODN probe	ΔV_{Gmin}/V	$I_{off\ (probe\text{-}modified\ film)}/I_{off\ (hybridization)}$	Number of transistors
HIV	−0.03 ± 0.02	3.4 ± 1.5	5
RAND	−0.04 ± 0.07	1.04 ± 0.04	5

presented in Table 3. This shows that hybridization is selective as a random target is discriminated.

3.2.3. Fluorescence experiments

To confirm that the changes in the transistor characteristics are due to ODN hybridization, a fluorescence study was performed (Fig. S5, Supplementary Information). As expected, after the washing steps, denaturation using DI water at 90 °C leads to a dramatic increase in the fluorescence intensity for the complementary target, whereas no significant change is visible for the random target. These results show that hybridization occurs selectively (25 pmol cm^{-2}) and that the semiconducting layer does not undergo significant unspecific adsorption (around 0.1 pmol cm^{-2}). This is an excellent results, as we have shown in a previous work that for positively-doped polymer if an amino group is present instead of carboxylate, then the unspecific adsorption resulting from electrostatic attractions is very high, reaching at least 500 pmol cm^{-2} [33,34]. Using DI water instead of PBS (Fig. S6) leads to exactly the same results, which demonstrates that DI water (during a relatively short period and at room temperature) does not lead to any significant denaturation; this supports the results obtained on the water-gated OFET.

4. Conclusion

The water-gated DNA OFET sensor is based on organic field-effect transistor in which the dielectric is constituted by a simple droplet of aqueous PBS solution, or, for best results, pure water. The advantage of this device is that a very high electric field is generated at the electrolyte/channel interface due to the formation of an electric double layer, allowing to operate at very low voltages (below 1 V). This renders possible the use of water or buffer solutions within their electrochemical stability window. As far as DNA detection is concerned, a P3HT derivative bearing carboxylic acid moieties was used to perform covalent ODN grafting. Clear changes in the electrical characteristics are observed upon DNA immobilization. The shift of the gate voltage of the minimum drain current towards negative values is attributed to the negative charge of the DNA backbone. The *off* current is also modified and decreases after DNA immobilization. This behavior is attributed to the steric hindrance of DNA chains that eventually prevents ion penetration into the bulk of the semiconductor [35]. These results point out the importance of the Debye length that can screen negative DNA charges. To address this screening issue, pure water was used instead of PBS solution in order to increase the Debye length. In this case, a decrease in the *off* current was observed upon hybridization whereas no significant change occurred when using PBS. Further experimental work is needed to fully understand the involved mechanisms.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2011.09.025.

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