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Technology Platform for Sampling Water with Electrolyte-Gated Organic Transistors Sensitised with Langmuir-Deposited Calixarene Surface Layers

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We demonstrate a technology platform that enables the development of new, surface-sensitised organic transistor sensors. We show that an organic semiconductor can still be gated by an electric double layer within the electrochemical window of water after the deposition of up to four Langmuir-Schäfer calixarene layers onto its surface. Since many calixarenes are known to selectively bind waterborne cations, this facilitates sensitising a conventional organic semiconductor with a physically deposited layer for specific cation recognition. When at least two Langmuir-Schäfer layers are deposited, these also block the electrochemical doping of the organic semiconductor, which otherwise competes with the field effect in water-gated organic transistors. Carrier mobility is reduced by the application of calixarene layers, but transistor current measurement remains accessible by simple methods. We find that for the present purpose, Langmuir-Schäfer-printed surface layers perform better than those deposited by Langmuir-Blodgett deposition.

Keywords: Polythiophene, Organic Transistor, Water, Electrolyte, Electric Double Layer, Langmuir-Blodgett, Langmuir-Schäfer, Calixarene, Surface, Sensitiser, Sensor.

1. INTRODUCTION

In the past decade, organic field-effect transistors (OFETs) have been increasingly applied as odour sensors for airborne analytes.^{1–4} Applications include environmental monitoring and the detection of illicit substances. Organic semiconductors offer unique potential for selective and specific interactions with analytes, and thus selective and specific sensor response. OFETs have also been used as sensors in the aqueous environment.^{5,6} Electric characterisation in water brings with it specific problems due to the conductivity of water, and its small electrochemical window of 1.23 V.⁷ Great care has to be taken to insulate the OFET's source and drain from electric contact with water, and low threshold transistors are favourable.

Here, we establish the technology platform for an alternative approach to water sampling with OFETs. This emerges from research using electrolytes, rather than insulators, to separate the OFET's semiconducting channel from the gate contact.^{8–10} Under an applied gate voltage, an electric double layer (EDL) forms at the

electrolyte/semiconductor interface, consisting of a carrier accumulation layer on the semiconductor side, and a layer of excess ions on the electrolyte side. EDLs are typically very thin (<1 nm), therefore EDL capacitance is high (a few $\mu\text{F}/\text{cm}^2$), albeit generally a complicated function of voltage, electrolyte concentration, and frequency.¹¹ Consequently, electrolyte-gated OFETs typically display very low thresholds in the order 0.2 V. Even deionised (DI) water is a weak electrolyte, partly due to autoprotolysis and partly due to carbonic acid resulting from dissolved atmospheric CO_2 .¹² Recently, Horowitz et al.¹³ have gated the organic semiconductor polythiophene with a droplet of DI water, and observed OFET behaviour with low threshold. However, a similar study by Inganäs et al.¹⁴ found that electrolyte-gated transistors may also display organic electrochemical transistor (OECT) behaviour,¹⁵ caused by the gate-driven electrochemical doping of the organic semiconductor, in parallel to field effect. The two phenomena can so far only be isolated by their different timescales.¹⁶ Also, further currents may be observed simultaneously, namely an ionic leakage current (I_{leak}) from source to drain across the water, albeit Horowitz et al. found leakage is largely reduced by covering source and drain contact

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Table I. The different currents found in electrolyte-gated organic transistors with hole-transporting organic semiconductor, and their I/V or $I(t)$ characteristics. V_S is a drive voltage applied to source, with drain and gate grounded. Biased currents are only observed during the 'on' half-cycle of the drive voltage, unbiased currents flow in the 'off' half-cycle, as well.

Type of current	Carrier	Caused by	Gate driven?	$I(V_S)$ or $I(t)$ characteristic
I_{OFET}	Holes	Field effect from electric double layer	Yes	$\sim(V_S - V_T)^2$
I_{OECT}	Holes	Electrochemical doping by ions from electrolyte	Yes	Slow increase with time (>10 ms to s)
I_{perm}	Holes	Permanent chemical dopants (e.g., catalyst residue)	No	$\sim V_S$ (ohmic)
I_{leak}	Ions	Non-perfect insulation btwn source/drain contacts and electrolyte	No	$\sim V_S$ (ohmic)

surfaces with a hydrophobic organic semiconducting polymer; and a current due to permanent doping (I_{perm}) in the organic semiconductor, which is an artefact of its synthesis, or exposure to oxygen. Both I_{leak} and I_{perm} are independent of gating. Table I summarises the currents that may flow in an electrolyte-gated organic transistor, and their characteristics.

Hence, using water as gate electrolyte in principle offers an attractive alternative for organic transistor-based water sampling, wherein the sample is a functional part of the sensor device. However, two major challenges remain. Firstly, organic semiconductors are not themselves specifically sensitive to particular ions. Gating requires either an anionic, or a cationic, EDL, depending on the type of organic semiconductor (anionic/cationic for a hole/electron transporter), but is otherwise indifferent to the chemical identity of the ion. Secondly, in water-gated organic semiconductors, there may be a number of other currents competing with field effect.

We here report on a technology platform designed to overcome these challenges. We introduce an ultrathin interface layer of Langmuir-deposited calixarenes at the organic semiconductor/water interface. A wide range of calixarenes are known that can selectively bind e.g., to particular cations,^{17,18} thus can specifically sensitise a water-gated transistor. Crucially, we show that a small number of Langmuir-deposited calixarene layers result in films thin enough not to compromise EDL gating, but can block the ionic doping currents that lead to OECT behaviour. We can delineate field effect from the other currents observed in water-gated devices, even when we use ordinary tap water rather than DI water as gate medium, to simulate a realistic environmental sample.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Water-Gated Transistors

A water-gated organic transistor is a relatively simple device, comprised of gold contacts, an organic semiconductor film, and a droplet of water with a gate contact needle inserted into it. Source-drain gold contacts (channel length $L = 10 \mu\text{m}$, and width $W = 2 \text{mm}$) were thermally evaporated on clean Si/SiO₂ substrates under 10^{-6} Torr vacuum through shadow masks. As organic semiconductor, we used two different batches of the common hole-transporting organic semiconductor, poly(3-hexylthiophene-2,5-diyl) (P3HT): one was purchased from Sigma-Aldrich (electronic grade 99.995%, average M_n 15000-45000), the other from Ossila (regioregularity 96.6%, average M_n 32000). Both materials showed similar performances, and are therefore not discussed separately. We dissolved 10 mg/mL of P3HT in dichlorobenzene (DCB) under stirring and heating to 60 °C for about 15 min, and filtered through a PTFE membrane syringe filter. We spin cast solutions (2000 rpm for 1 min) onto the described substrates. Cast films were dried under dynamic vacuum at 40 °C for 1 h. As model calixarene, we used the nitro-ester calix[4]arene (5,17-(34-nitrobenzylideneamino)-11,23-di-tert-butyl-25,27-diethoxycarbonyl methyleneoxy-26,28-dihydroxy calix[4]arene), shown in the inset of Figure 1, synthesized as described previously.¹⁹ The calixarene was diluted in chloroform (0.1 mg/mL) and 350 μL of solution were spread on the water surface of a Langmuir trough (Nima 611D Standard Trough) to form a monolayer. Langmuir isotherms (Fig. 1) were recorded using Nima software. Compressed calixarene films collapsed at a surface pressure of ~ 40 mN/m, hence we deposited calixarene films by either the Langmuir-Blodgett (LB) deposition technique, or Langmuir-Schäfer (LS) printing technique (Fig. 2), at slightly lower surface pressure, ~ 35 mN/m, to prepare dense layers. To represent an environmental water sample, we used local tap water without purification. We placed a 2 μL droplet of tap water on the channel with the help of a

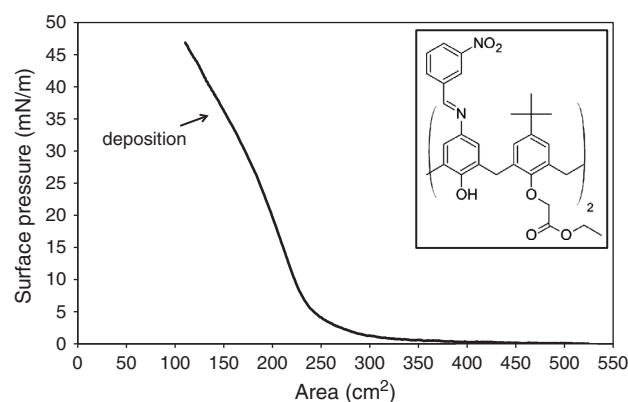


Fig. 1. Langmuir isotherm of the calixarene used as ultrathin interfacial layer, chemical structure in the right-side inset.

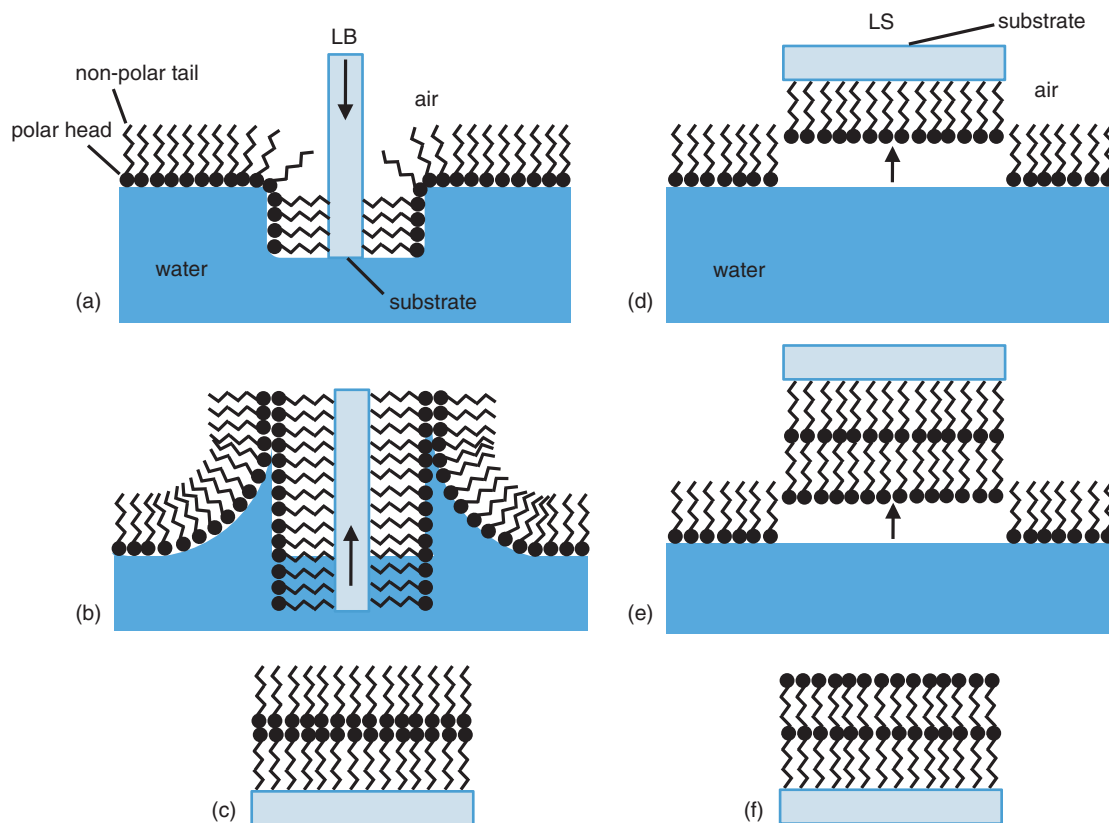


Fig. 2. Comparison between Langmuir-Blodgett (LB) and Langmuir-Schäfer (LS) films. (a–b) and (d–f) depict the two steps for a two layer-deposition for LB and LS, respectively. The immersion (a) and emersion (b) of the substrate result in a LB film (c) in which the second layer of particles is disposed in the opposite way with respect to the LS film (f), obtained after two consecutive dips, (d) and (e).

micro-litre syringe, and inserted a tungsten (W) needle as gate contact. Source and drain were also contacted with W needles, avoiding direct contact with the droplet. Figure 3 shows the overall device architecture.

2.2. Characterisation

We have shown recently that ‘dry’ gated organic transistors can be reliably and comprehensively characterised by a simple current/voltage (I/V) converter circuit (shown in the right inset of Fig. 3) and suitable AC electric drive protocol, which maps out the saturated transfer characteristics.²⁰ Here, we have adapted this method for the characterisation of water-gated transistors. To minimise parasitic capacitive currents, we applied lower frequency (1 Hz) drive voltages (V_S) with amplitude $V_{MAX} = 0.8$ V to the OFET source, using either square or sine waveforms. Gate needle was grounded, and drain was on virtual ground of an I/V converter with dial-in feedback resistance, R_f . The transistor’s drain current, I_D , is thus converted into an output voltage, V_{OUT} , according to $V_{OUT} = -R_f I_D$. Input and output signals were recorded on a storage oscilloscope, and R_f was chosen to match the maximum of $-10V_{OUT}$ to V_{MAX} . Some samples delivered low currents that showed contributions from 50 Hz mains

‘hum’; for the characteristics obtained under sine drive this could be effectively filtered using LabView (fast Fourier transform/50 Hz notch filter/inverse Fourier transform); under square wave drive, a median filter was more effective. We found that the competition between field effect and electrochemical doping, and the OFET on/off ratio, are easily evaluated from the results under square wave drive, while OFET threshold and carrier mobility are more readily read from results under sine drive. First, we determined threshold voltage (V_T) as described in Ref. [20], then calculated the product of carrier mobility and specific capacitance of the EDL, μC_i , according to:

$$\mu C_i = \frac{2L}{WR_f} \frac{|V_p|}{(V_{MAX} - |V_T|)^2} \quad (1)$$

where L/W is the transistor channel length/width, R_f the feedback resistance, V_{MAX} , V_p are the maxima of the drive/output voltage (here, 0.8 and 0.08 V, respectively). We prefer quoting μC_i rather than μ , due to the difficulties with finding a precise value for C_i of an EDL;¹¹ Horowitz et al. estimate $C_i \approx 3 \mu\text{F}/\text{cm}^2$ for DI water at low frequency.¹³ To check for consistency, we have also recorded output characteristics of water-gated transistors using conventional source/measure units on a few examples. Characteristics were very similar to those reported

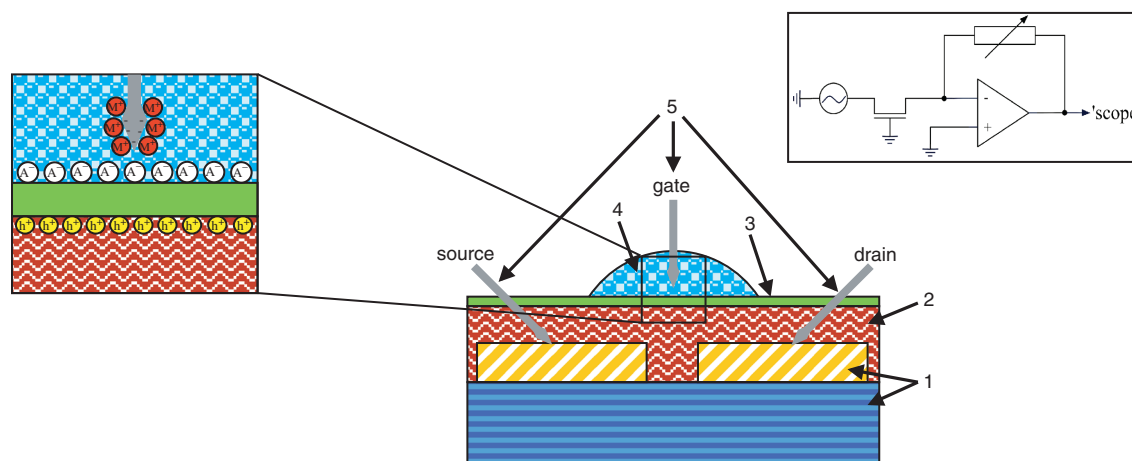


Fig. 3. A calixarene-sensitised, water-gated transistor, shown schematically. (1) Si/SiO₂ substrate and Au contacts; (2) P3HT layer; (3) Calixarene film; (4) Water sample; (5) Gate contact. The inset on the left is an enlargement of the calixarene-sensitised interface under positive source voltage, showing a cationic EDL at the water/sensitiser interface, and a corresponding hole accumulation layer at the semiconductor/sensitiser interface. The inset on the right shows the electronic circuit we used to drive and measure water-gated transistors.

by Horowitz et al. and we extracted similar thresholds and μC_i as under sine drive/ I/V converter characterisation.

3. RESULTS AND DISCUSSION

Figures 4(a) and (b) show the drive voltage, V_S , and the drain current, I_D , (derived from V_{OUT}) under square and

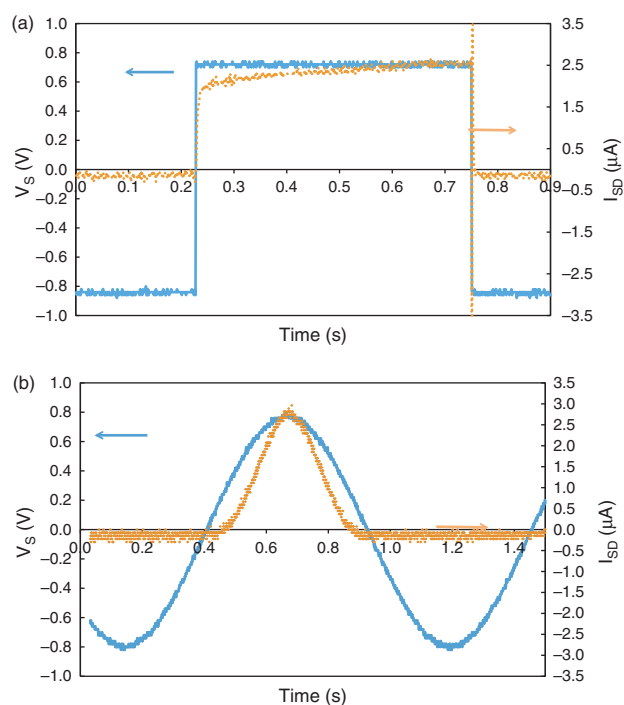


Fig. 4. AC characterisation of a P3HT uncoated transistor: square-wave drive (a) and sine-wave drive (b). The blue signal is the input voltage, V_S , and the orange is the drain current, I_D , derived from the output voltage, V_{OUT} .

sine wave drive, respectively, of a water-gated OFET without any calixarene surface layers. Under square wave drive (4a), in the positive V_S half-cycle, we find I_D initially ‘jumps’, then slowly increases further over time, until V_S is reversed. This signal reveals contributions from both field effect and electrochemical transistor behavior: the initial quick jump is a response to field effect (I_{OFET} , which takes less than 10 ms to appear), and then electrochemical doping gives rise to a slowly increasing current, I_{OECT} . These observations are very similar to those by Inganäs et al.¹⁶ In the negative V_S (‘off’) half-cycle, contributions from both field effect and electrochemical doping are zero; however, a small I_D is nevertheless observed. This reveals contributions from either, or both, ionic leakage currents from source to drain across water (I_{leak}), and permanent doping of the organic semiconductor (I_{perm}), cf. Table I. These currents are also present during the positive (‘on’) half cycle, adding to the transistor currents, however this is unimportant as long as they are comparatively small. Under sine wave drive (4b), characteristics look very similar to those observed for ‘dry’ transistors under similar conditions.²⁰ We extract the ratio of field-effect to electrochemical current (I_{OFET}/I_{OECT}), and the transistor’s on/off ratio, from Figure 4(a), and threshold (V_T) and μC_i from Figure 4(b) and Eq. (1). All characteristics of this transistor are summarised in the first row of Table I.

Figure 5 shows the corresponding result for a water-gated OFET where the P3HT surface had first been coated by 4 LS layers of the calix[4]arene, inset Figure 1. Figure 5(a) shows that current on/off ratio is significantly reduced; this is not due to a significant increase of the off-currents (I_{perm} , I_{leak}), but due to a reduction of ‘on’ currents, note the different current scales in Figures 4 and 5. We conclude that the application of the LS layers has significantly reduced carrier mobility in the accumulation layer, which affects the transistor currents, but not dop-

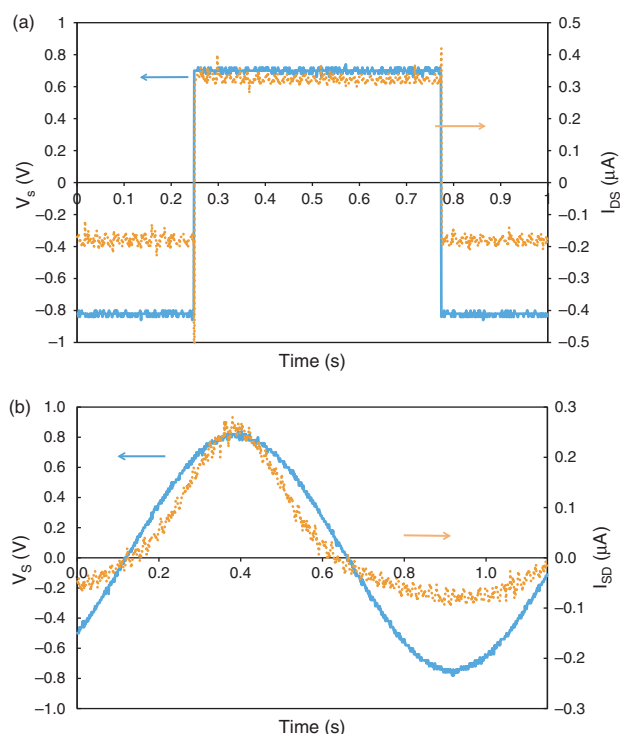


Fig. 5. AC characterisation of a P3HT transistor coated with four LS layers: square-wave drive (a) and sine-wave drive (b). The blue signal is the input voltage, V_S , and the orange is the drain current, I_D , derived from the output voltage, V_{OUT} . FFT filtering was applied to 4b.

ing or leakage current. Figure 5(a) also shows that current in the 'on' half-cycle now no longer slowly increases with time. We conclude the 4 LS layers block the gate-driven flow of ions from the electrolyte into the semiconductor, hence I_{OECT} is suppressed. To calculate threshold, and μC_i , from Figure 5(b), we have first subtracted the current observed during the 'off' (negative V_S) half-cycle from the 'on' current, to correct for contributions from I_{leak} and/or I_{perm} , before evaluating V_T and μC_i . We find that threshold is in fact reduced as a result of applying 4 LS layers to the P3HT surface, which implies that 4 calixarene LS layers are thin enough not to compromise the high capacitance of the EDL. However, as we already concluded from comparison of Figures 5(a) to 4(a), mobility in the accumulation layer is substantially reduced, about 18-fold on the assumption that C_i is not affected by the LS layers. Data are summarised in the 2nd row of Table II. We carried out similar studies for transistors coated with two and one LS calixarene layers, instead of four. Resulting transistor characteristics looked similar to those shown in Figure 5, and were evaluated in the same way, to give the data shown in rows 3 and 4 of Table II. Data and conclusions for 2 LS layers are very similar to those for 4 calixarene LS layers; for 1 LS layer we find that the blockade of electrochemical doping is no longer complete, although the I_{OECT}/I_{OFET} ratio is still smaller than without LS coating.

Table II. Data read and derived from AC characterisation for uncoated and coated transistors. Columns 1, 2 are read from transistor currents under square-wave drive. Column 1 gives the relative contributions to 'on' current from electrochemical doping. Column 2 gives the transistor's on/off ratio. Columns 3, 4 are read (V_T , column 3), or calculated (μC_i , column 4, using Eq. (1)) from currents under sine drive.

Sample	I_{OECT}/I_{OFET}	I_{on}/I_{off}	V_T (V)	$10^9 \mu C_i$ ($CV^{-1}s^{-1}$)
Uncoated P3HT	0.31 ± 0.03	19.8 ± 1.80	0.28 ± 0.03	113 ± 14.0
4LS-coated P3HT	0	3.33 ± 0.30	0.16 ± 0.02	6.35 ± 0.8
2LS-coated P3HT	0	2.50 ± 0.25	0.14 ± 0.01	5.74 ± 0.7
1LS-coated P3HT	0.13 ± 0.01	1.60 ± 0.15	0.10 ± 0.01	3.82 ± 0.5
4LB-coated P3HT	0.42 ± 0.04	4.22 ± 0.40	0.38 ± 0.04	3.97 ± 0.5

When a transistor is coated with four layers of calixarene through LB deposition, rather than LS printing, we observe a different behaviour compared to the LS samples. Electric characteristics are shown in Figure 6 and are evaluated in the same way as before to give the final row in Table II. Again, carrier mobility is significantly reduced, and threshold now is increased compared to the uncoated sample. Also, even 4 LB layers cannot completely block electrochemical doping. The LB-coated transistors are also harder to work with practically, as the surface is rather hydrophobic, and the gating water droplet tends to run off the surface. This is explained due to the different orienta-

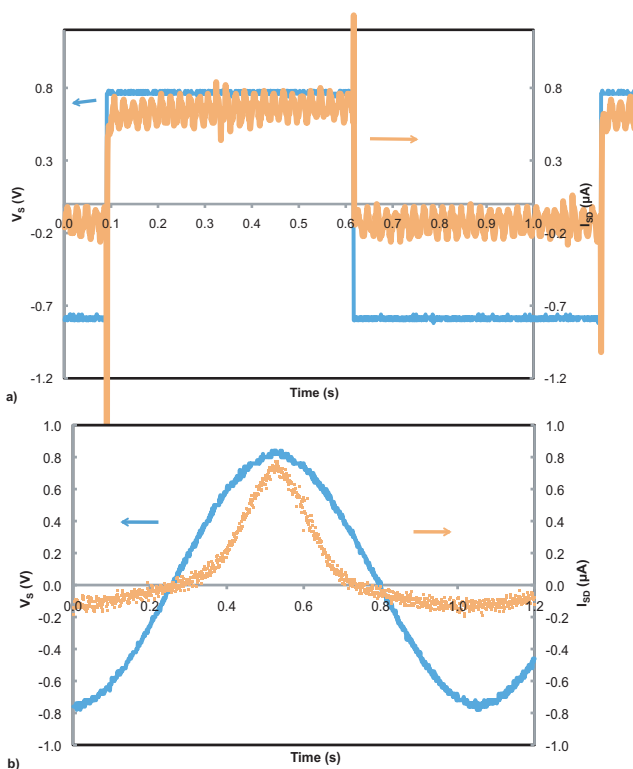


Fig. 6. AC characterisation of a P3HT transistor coated with four LB layers: square-wave drive (a) and sine-wave drive (b). The blue signal is the input voltage, V_S , and the orange is the drain current, I_D , derived from the output voltage, V_{OUT} .

tion of calixarenes in LB films, compared to LS films;²¹ LB films present the hydrophobic upper rim to the surface, while LS films present the hydrophilic lower rim (Figs. 2(c and f)).

4. SUMMARY AND CONCLUSIONS

We demonstrate a technology platform that enables the development of new organic transistor sensors. We show that an organic semiconductor can still be water-gated within the electrochemical window of water even after the Langmuir deposition of up to four calixarene layers to its surface, because such layers are thin enough not to compromise the high capacitance of an electric double layer. Since many calixarenes are known to selectively bind waterborne cations, this allows sensitising a conventional organic semiconductor with a physically deposited layer for the specific recognition of waterborne cations. Thus the functionalities required for transistor sensors, i.e., charge carrier transport, and specific recognition, can be met by combining currently known materials by physical deposition methods, without the need for synthesis of new materials with dual functionality, or chemical grafting of sensitisers onto semiconductor films. When two or more LS (rather than LB) layers are deposited, these block the electrochemical doping of the organic semiconductor, which usually competes with field effect in water-gated organic transistors. Since electrochemical doping is not specific to the chemical identity of the doping ion, such doping is parasitic with respect to ion recognition, and the observed blockade is a desirable feature, which can be achieved by as few as 2 LS layers. Since LS films also wet better than LB films, we therefore recommend LS printing over LB dipping as the method-of-choice for the sensitising of organic semiconductors. Water-gated transistor characteristics are easily recorded with a simple measurement setup, that only requires cheap and widely available equipment (signal generator, OpAmp, resistance box, and storage oscilloscope). Data may require some processing (filtering 50 Hz hum, subtraction of 'off'-current) before they can be analysed, but processing, as well as extraction of mobility and threshold, are straightforward. It is currently unknown why LS (but not LB) films block ionic doping currents, and why carrier mobility is reduced by the application of calixarene interface layers.

Future work will address the remaining drawback of the method developed so far: the organic semiconductor P3HT we used here is a hole transporting material, and therefore turns 'on' under an anionic EDL, while most reported calixarenes selectively bind cations. We therefore need to replace P3HT with an electron-transporting material, which implies problems, because hydroxyl (-OH) groups are known as electron traps, and -OH groups are present both at the lower rim of the calixarene, and water. However, high electron affinity electron transporters (LUMO

below 3.8 eV) have been reported to be not susceptible to such traps,²² and such materials are now commercially available.²³ For such devices, we expect a strong impact on the measured transistor characteristics when a 'target' cation binds to a sensitiser calixarene. In particular, we expect hysteresis, as bound cations will continue to sustain a carrier accumulation layer at the semiconductor surface even after V_g has dropped back below threshold.

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