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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.

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Electron transporting water-gated thin film transistors

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Organic solvents as gate media for thin-film transistors

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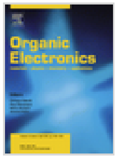

Water-gated organic nanowire transistors

The remaining authors report with great sadness the passing of our co-author Tim Richardson shortly before publication. We wish to dedicate this work to the memory of a much missed colleague and friend.

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The University Of Sheffield.

Progress in electrolyte- gated thin film transistors

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SID ORGANIC ELECTRONICS UK 2012
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1. Introduction

In recent years, it has been shown that thin film transistors (TFTs) can be gated via an electrolyte due to the high capacitance electric double layer (EDL) that forms at the electrolyte/semiconductor interface under applied gate bias. In particular the observation of Kergoat *et al.*[1] that an organic TFT can be gated by pure-water has generated a great interest in using such devices in the sensing of aqueous-analytes.

Here, we demonstrate an electron-transporting water-gated TFT, using thermally converted precursor-route Zinc Oxide (ZnO), as seen in fig.1. Also, we show that some organic solvents, can act as EDL gate media for TFTs, in a similar way as solid electrolytes, ionic liquids, and water itself. We demonstrate this for both p- and n-type TFTs. Finally, we demonstrate electrolyte-gated organic NW field-effect TFTs using NWs grown from both p-type, and n-type, Organic Semi-conductors OSCs such as nano-belts of BBL for n-type, and nano-wires of PBTTT and P3HT for p-type

2. Materials and Method

Zinc acetate dihydrate ($Zn(OAc)_2$) in ethanol is converted into **ZnO**. It shows ZnO here is largely an intrinsic semiconductor, just like sputtered ZnO [2] . We have treated the ZnO surface of such samples to turn them hydrophobic. This was either by spin casting **HMDS** or one layer of **stearic acid** by the Langmuir-Schäfer (LS) technique [3]. For gating n-type nano-belts, we have selected poly(benzimidazo-benzophenanthroline) (**BBL**) that possesses a rather deep 'lowest unoccupied molecular orbital' (LUMO) of - 4.0 eV [4]. As suggested from Nicolai H.T. et al. [5], the only way to avoid traps is to possess polymers that its LUMO levels are lower than 3.6 eV below vacuum level. Nanowire growth: '**CB-P3HT**' NWs were grown in Cholorobenzene poly(3-hexylthiophene), rrP3HT, and '**Anisole-P3HT**' NWs were prepared via a variation on the whisker method [6]. (sourced from Ossila)

3. Overview Fabrication

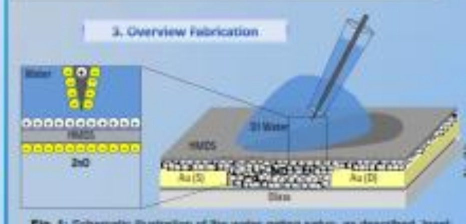

Fig. 1: Schematic illustration of the water gating setup, as described. Inset: Positive bias applied to gate needle leads to an electron accumulation layer at the ZnO surface. Also the anionic EDL in the water near the gate needle, and the cationic EDL in the water near the ZnO surface

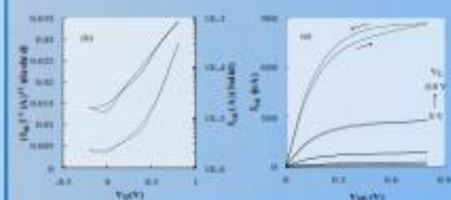

Fig. 2: Output (2a)-and saturated transfer (2b) characteristics of water-gated HMDS-ZnO TFTs. In Fig. 3b, the source-drain voltage for the saturated transfer characteristics was 0.9 V.

4. Processing and Characterisation

For isotherm and LS deposition, a **NIMA Langmuir trough** (Model 611) was used. To record TFT output- and transfer characteristics, we used two **Keithley 2400** source/measure units. **I/V convertor** unit is used to measure the real-time characterisation of on-current, off-current and other vital parameters such as threshold and mobility, as described in [7, 8].

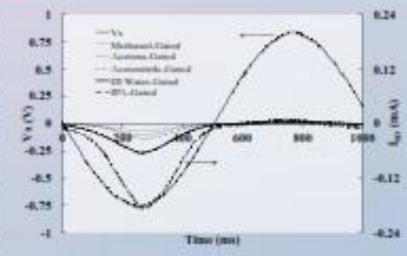

Fig. 3: Sinusoidal drive voltage Vx (amplitude 0.8V, f = 1Hz), and resulting saturated drain current (I_{SD}), for ZnO TFTs gated with water, and several organic solvents. I_{SD} under water- gating is downscaled 10- fold to fit on the same scale.

	Water	Methanol	IPA	Acet-one	Aceto-nitrile	Chloro-form	Tolu-ene	Cyclo-hexane
pK_a	14	16.6	20.7	>32.5	∞	∞	∞	∞
Dipole [D]	1.85	1.7	1.66	2.88	3.92	1.04	0.36	0
H_2O sol. [g/L]	-	misc.	misc.	misc.	misc.	8	0.47	~0
ZnO	Y- (Y+)	Y-	Y- (Y+)	Y-	Y-	N	N	N
I_{on} [%]	100	2.5	28.5	3.9	5.1	0	0	0
P3HT	Y+	Y+	Y+	Y+	Y+	X	X	N
I_{on} [%]	100	12.7	8.5	5.8	11.8	X	X	0
PBTTT	Y+	Y+	Y+	Y+	Y+	X	X	N
I_{on} [%]	100	13.2	6.6	5.1	14.3	X	X	0

Table 1: Summary of physicochemical properties of the solvents used here, and results for attempting to gate different semiconductors with different solvents. pKa for autoprotolysis at 25 °C from [9]; solvents that cannot undergo autoprotolysis have infinite pKa. Molecular dipole moments (in Debye) from [10]. Solubility in water in g of solvent per Litre of water; 'misc.' indicates miscibility in any ratio. Y- / Y+: Electron / hole field effect current was observed under applied gate voltage. (Y+): Small hole current. N: No current.

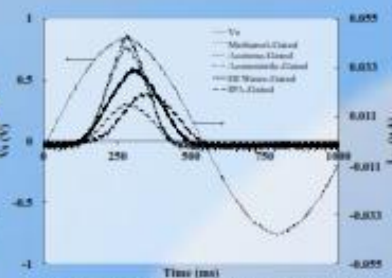

Fig 4: Sinusoidal drive voltage Vx (amplitude 0.8V, f = 1Hz), and resulting saturated drain current (I_{SD}), for PBTTT TFTs gated with water, and several organic solvents. I_{SD} under water-gating is downscaled 10- fold to fit on the same scale.

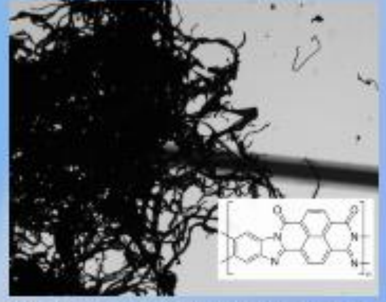

Fig. 5: Optical micrograph of BBL 'nanobelts' on TFT substrate, and twin-twisted nanobelts form increases width/diameter of nanobelts. It has been deposited on gold contacts that thermally evaporated on SiO_2 . Insert: the molecular structure of BBL that been used here.

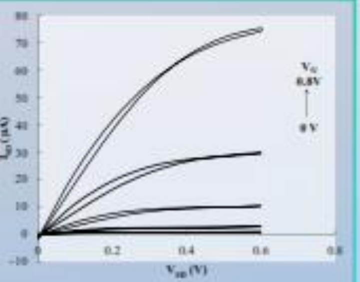

Fig. 6: Output characteristic of BBL nanobelt film gated with water, immediately after applying the gate droplet of Acetonitrile. It works for just 6 mins.

5. Conclusion

- Water gated HMDS-ZnO TFTs display low threshold and high electron mobility. Moreover, Gate geometry is relevant for optimum performance of water- gated TFTs.
- We recommend the use of L-shaped electrodes that overlap the width of the TFT channel with leaving a water gap in the order of 0.1 mm.
- We find that organic solvents that are miscible with water (i.e., polar organic solvents) can act as EDL gate media for thin film transistors, in a similar way as previously reported for water. The most likely explanation for the ability to act as EDL gate medium is the inevitable presence of trace amounts of dissolved salts in such solvents.
- Acetonitrile in particular is an attractive alternative gate medium to water.
- Acetonitrile gating avoids -OH groups in the gate medium that are known to act as charge carrier traps [11], and offers a wider electrochemical window than water [12].
- We have demonstrated the first water-gated n-type and p-type organic nanowire field-effect devices.
- For the application of interfacial sensitisers, the polar (hydrophilic) ZnO surface may be an advantage over organic semiconductor surfaces. Electron transporting TFT transducers would be particularly suited for the detection of cationic waterborne species.

6. Acknowledgements

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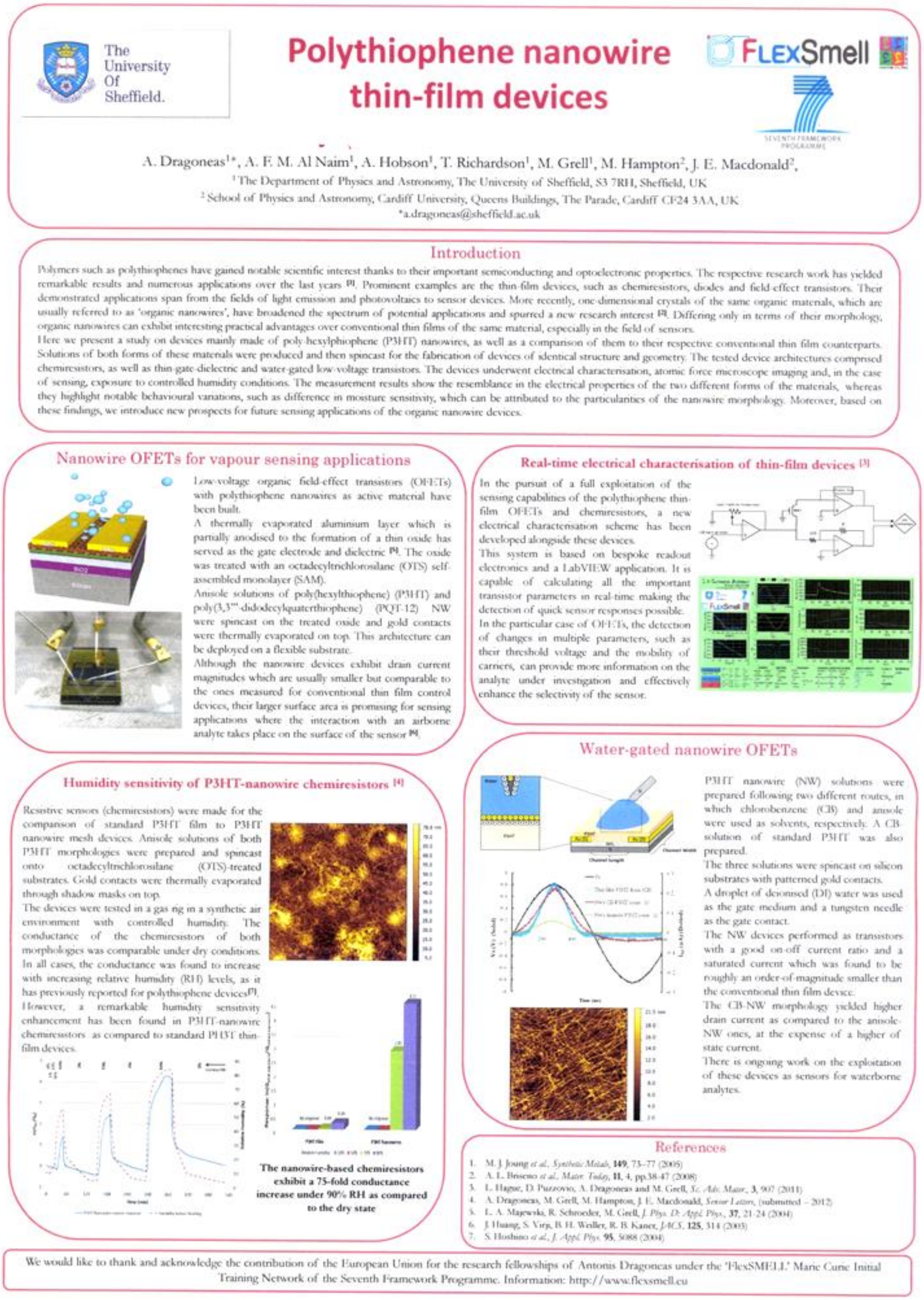
Second Poster: (presented by my colleague in 2012 MRS Fall Meeting & Exhibit on November 25 - 30, 2012, Boston, MA, USA).



Polythiophene nanowire thin-film devices

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Introduction

Polymers such as polythiophenes have gained notable scientific interest thanks to their important semiconducting and optoelectronic properties. The respective research work has yielded remarkable results and numerous applications over the last years [1]. Prominent examples are the thin-film devices, such as chemiresistors, diodes and field-effect transistors. Their demonstrated applications span from the fields of light emission and photovoltaics to sensor devices. More recently, one-dimensional crystals of the same organic materials, which are usually referred to as 'organic nanowires', have broadened the spectrum of potential applications and spurred a new research interest [2]. Differing only in terms of their morphology, organic nanowires can exhibit interesting practical advantages over conventional thin films of the same material, especially in the field of sensors.

Here we present a study on devices mainly made of poly-hexylphiophene (P3HT) nanowires, as well as a comparison of them to their respective conventional thin film counterparts. Solutions of both forms of these materials were produced and then spincast for the fabrication of devices of identical structure and geometry. The tested device architectures comprised chemiresistors, as well as thin-gate-dielectric and water-gated low-voltage transistors. The devices underwent electrical characterisation, atomic force microscope imaging and, in the case of sensing, exposure to controlled humidity conditions. The measurement results show the resemblance in the electrical properties of the two different forms of the materials, whereas they highlight notable behavioural variations, such as difference in moisture sensitivity, which can be attributed to the particularities of the nanowire morphology. Moreover, based on these findings, we introduce new prospects for future sensing applications of the organic nanowire devices.

Nanowire OFETs for vapour sensing applications

Low-voltage organic field-effect transistors (OFETs) with polythiophene nanowires as active material have been built.

A thermally evaporated aluminium layer which is partially anodised to the formation of a thin oxide has served as the gate electrode and dielectric [5]. The oxide was treated with an octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM).

Anisole solutions of poly(hexylthiophene) (P3HT) and poly(3,3'''-didodecylquaterthiophene) (PQT-12) NW were spincast on the treated oxide and gold contacts were thermally evaporated on top. This architecture can be deployed on a flexible substrate.

Although the nanowire devices exhibit drain current magnitudes which are usually smaller but comparable to the ones measured for conventional thin film control devices, their larger surface area is promising for sensing applications where the interaction with an airborne analyte takes place on the surface of the sensor [6].

Real-time electrical characterisation of thin-film devices [3]

In the pursuit of a full exploitation of the sensing capabilities of the polythiophene thin-film OFETs and chemiresistors, a new electrical characterisation scheme has been developed alongside these devices.

This system is based on bespoke readout electronics and a LabVIEW application. It is capable of calculating all the important transistor parameters in real-time making the detection of quick sensor responses possible.

In the particular case of OFETs, the detection of changes in multiple parameters, such as their threshold voltage and the mobility of carriers, can provide more information on the analyte under investigation and effectively enhance the selectivity of the sensor.

Humidity sensitivity of P3HT-nanowire chemiresistors [4]

Resistive sensors (chemiresistors) were made for the comparison of standard P3HT film to P3HT nanowire mesh devices. Anisole solutions of both P3HT morphologies were prepared and spincast onto octadecyltrichlorosilane (OTS)-treated substrates. Gold contacts were thermally evaporated through shadow masks on top.

The devices were tested in a gas rig in a synthetic air environment with controlled humidity. The conductance of the chemiresistors of both morphologies was comparable under dry conditions. In all cases, the conductance was found to increase with increasing relative humidity (RH) levels, as it has previously reported for polythiophene devices[7].

However, a remarkable humidity sensitivity enhancement has been found in P3HT-nanowire chemiresistors as compared to standard PH3T thin-film devices.

The nanowire-based chemiresistors exhibit a 75-fold conductance increase under 90% RH as compared to the dry state

Water-gated nanowire OFETs

P3HT nanowire (NW) solutions were prepared following two different routes, in which chlorobenzene (CB) and anisole were used as solvents, respectively. A CB-solution of standard P3HT was also prepared.

The three solutions were spincast on silicon substrates with patterned gold contacts.

A droplet of deionised (DI) water was used as the gate medium and a tungsten needle as the gate contact.

The NW devices performed as transistors with a good on-off current ratio and a saturated current which was found to be roughly an order-of-magnitude smaller than the conventional thin film device.

The CB-NW morphology yielded higher drain current as compared to the anisole-NW ones, at the expense of a higher of state current.

There is ongoing work on the exploitation of these devices as sensors for waterborne analytes.

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