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A water-gated organic thin film transistor as a sensor for water-borne amines

Saud A. Algarni [a,*], Talal M. Althagafi [a], Abdullah Al Naim [b], Martin Grell [a]

[a] Physics & Astronomy, University of Sheffield, Hicks Building, Hounsfield Rd, Sheffield S3 7RH, UK
[b] Physics department, King Faisal University, Al-Ahsa, Saudi Arabia

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ABSTRACT

The p-type semiconducting polymer *Poly*(2,5-*bis*(3-*hexadecylthiophen*-2-*yl*)*thieno*[3,2-*b*]*thiophene*) (PBTTT) displays innate sensitivity to water-borne amines. We demonstrate this with the help of water-gated PBTTT thin film transistors (TFTs). When octylamine is added to the gating water, TFTs respond with a significantly reduced saturated drain current. Underlying TFT drift is minimised by initial conditioning, and remaining drift can be accounted for by normalising current response to the current level under purge immediately before exposure. Normalised current response *vs.* amine concentration is reproducible between different transistors, and can be modelled by a Langmuir surface adsorption isotherm, which suggests physisorption of analyte at the PBTTT surface, rather than bulk penetration. Same PBTTT transistors do not respond to 1- octanol, confirming the specific affinity between amines and thiophene- based organic semiconductors.

1. Introduction

Proteins are a key ingredient of food, and are found *e.g.* in meat, fish, and dairy products. Food spoilage includes the breakdown of proteins and the release of amines as breakdown products [1]. Hence, amine sensors are an important tool to assess the freshness (or otherwise) of food.

It was shown previously that organic conductors may respond to (airborne) amine odours. Sotzing et al. [2] demonstrated a chemiresistor that was highly sensitive and selective to amine odours based on a sulphonic acid-doped poly(aniline) (PAni) synthetic metal/carbon black composite. Resistivity substantially increased under odour exposure due to the de-doping of the acid-doped PAni by the amine acting as a Lewis base. Similarly, Hague et al. [3] demonstrated an organic transistor-based sensor for amine odours where a previously un-doped n-type organic semiconductor was doped by amine odours, with consequential impact on transistor characteristics [4–9].

We here extend this sensitivity of organic semiconductors to amines to the sensing of water-borne amines. Our sensor concept builds on the discovery of Berggren et al. [10] that organic thin film transistors (OTFTs) can be gated using water as an electrolytic gate medium. A number of works have since been published where water-borne analytes have been detected by monitoring the characteristics of water-gated OTFTs when analyte at different concentrations was added to the aqueous gate medium [11–14]. Such sensors typically rely in the sensitising of the OTFT with an analyte-specific receptor.

We here instead use the innate sensitivity of organic semiconductors to amines to demonstrate sensing of water-borne amine with a water-gated organic TFT.

2. Material and methods

2.1. Transistors

OTFTs were formed in a modular 'sandwich' flow cell design that results from mating two parts face-to-face with a Kapton spacer to establish a channel for water flow with dimensions 13 mm length, 5 mm width, 240 μm thickness; 15.6 μL volume (Fig. 1a). The first part consisted of 5 gold (Au) Source/Drain contact pairs (contact width $W=1$ mm separated by $L=30$ μm, $W/L=33.33$; 120 nm Au evaporated onto 5 nm Cr as an adhesion layer) on 20 mm × 15 mm rectangular glass substrates that were coated with the p-type semiconducting polymer *Poly*(2,5-*bis*(3-*hexadecylthiophen*-2-*yl*)*thieno*[3,2-*b*]*thiophene*) (PBTTT) sourced from Ossila Ltd. and spincast from 7 mg/mL hot solution (~100 °C) in 1,2-Dichlorobenzene (5000 rpm for 40 s), and then dried under dynamic vacuum at 110 °C for 45 min. PBTTT is known to perform well in water-gated OTFTs [15]. The second part consisted of a similar glass substrate with a central 1.5 mm wide gate strip

* Corresponding author.
E-mail address: php11saa@sheffield.ac.uk (S.A. Algarni).

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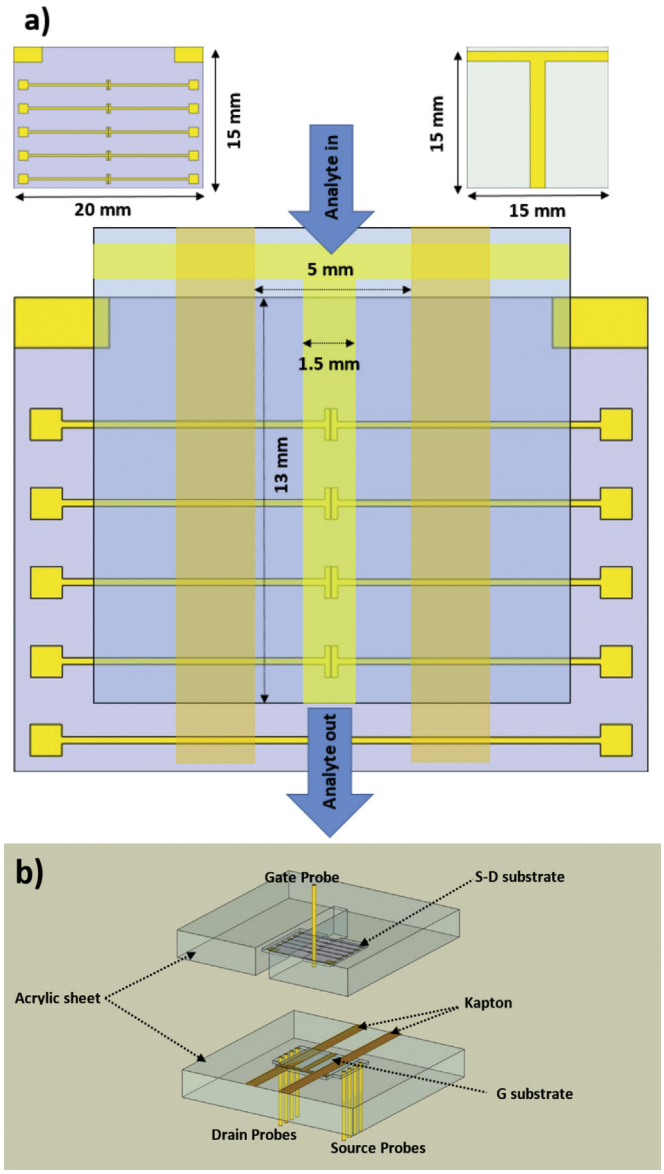

Fig. 1. PBTTT thin film transistors. (a) 'Sandwich' flow cell: five Au source/drain contact pairs and T-shaped Au gate contact on separate substrates are mated face-to face with a Kapton spacer. (b) The flow cell is held together by acrylic sheets with machined recesses to hold substrates, and S, D and G are electrically contacted by Au needles.

(evaporated Au with Cr adhesion layer) to overlap the S/D contact pairs on the first substrate. Fig. 1a shows the sandwich flow cell assembly which is held together by an acrylic box, which also prevents wetting of the electric contacts with aqueous analyte.

2.2. Analyte delivery

We used two NE-300 Just Infusion™ Syringe Pumps from New Era Pump Systems, Inc. to drive two 60 mL syringes in parallel with separately adjustable speeds. One syringe was filled with DI water, the other with a saturated solution of octylamine in DI water as an example amine, or with a saturated aqueous solution of the analogous alcohol 1-octanol for control experiments. Octylamine and 1-octanol were sourced from Aldrich, aqueous solutions saturate at 1.54 mM at 25 °C for octylamine, and 3.53 mM for 1-octanol [16]. Syringes were coupled to PEEK GPC tubing (0.51 mm inner diameter) from Kinesis Scientific Experts, and flows were mixed in a Y-coupler equipped with one- way valves to avoid back flow. The total dead volume of the delivery system was 41 µL. The sum of the pump rates of both pumps was kept constant at 250 µL/min throughout, but the ratio of pump rates is varied to vary analyte concentration in the resulting mixture. Hence the sensing systems' total (flow cell+tubing) dead volume was turned over in less than 14 s. The mixture is fed into the flow channel of the 'sandwich' cell via a syringe needle with 0.23 mm outside diameter, flow cells are drained on the other side with the help of a Kapton spacer channel then dripped into a waste reservoir. Fig. 2 shows a sketch of the analyte delivery system.

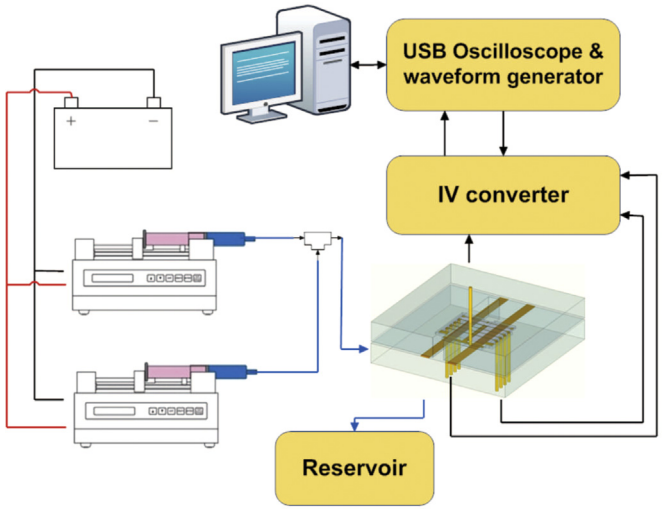

Fig. 2. Sketch of analyte delivery system for octylamine sensing.

2.3. Electrical characterisation

Flow cell OTFTs were linked to a real time electrical characterisation system wherein they are driven by a ± 1 V sinusoidal drive voltage at $f=1$ Hz applied to source, with gate grounded and resulting drain current sunk into the virtual ground of a current/voltage converter. In this setup, a positive source voltage is equivalent to a grounded source with negative and equal gate- and drain-voltages in a conventional semiconductor parameter analyser, and will turn a hole-transporting OTFT 'on' into drain current saturation when threshold is exceeded. We have described this characterisation scheme in detail in an earlier publication [17]. Gating is affected across water as this acts as electrolyte, as previously described by Berggren et al. [10]. Data were recorded every second in the form of peak drain current ('on- current' at $V_S=1$ V) *vs*. time; 'off current' (at $V_S=-1$ V) was also recorded.

3. Results and discussion

Fig. 3 shows the 'on-current' of a flow cell transistor under continuous pumping with plain DI water over ~2 h. Data show low noise but OTFT peak drain current continuously drifts from an initially large negative value of 480 nA at 1 V source voltage towards lower values, approaching (147 ± 10)nA that no longer drifts after 1 h. We assign this drift to a 'washing' of water soluble dopants out of PBTTT. A small number of unintentional dopants is always present in any organic semiconductor. While these dopants carry only a small current (the transistor's off-current), dopants can significantly improve carrier injection at the contacts by forming Schottky junctions [18]; loss of dopants may therefore lead to reduced injection.

Fig. 4a shows a similar chart for a PBTTT OTFT that has previously been conditioned by < 1 h 'washing' under continuous DI