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

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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.

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 sulfonic 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.

Material and methods

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 $13mm$ length, $5mm$ width, $240\mu m$ thickness; $15.6\mu L$ volume (Fig.1a). The first part consisted of 5 gold (Au) Source/Drain contact pairs (contact width $W = 1\ mm$ separated by $L = 30\ \mu m$, $W/L = 33.33$; $120nm$ Au evaporated onto $5nm$ Cr as an adhesion layer) on $20mm$ x $15mm$ 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 ^{o}C) in 1,2-Dichlorobenzene (5000 rpm for 40 $seconds$), and then dried under dynamic vacuum at 110 ^{o}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 $1.5mm$ wide gate strip (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.

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 ^{o}C for octylamine, and 3.53 mM for 1-octanol [16]. Syringes were coupled to PEEK GPC tubing (0.51mm 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 41μL. The sum of the pump rates of both pumps was kept constant at 250 $\mu L/minute$ 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 0.23mm 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.
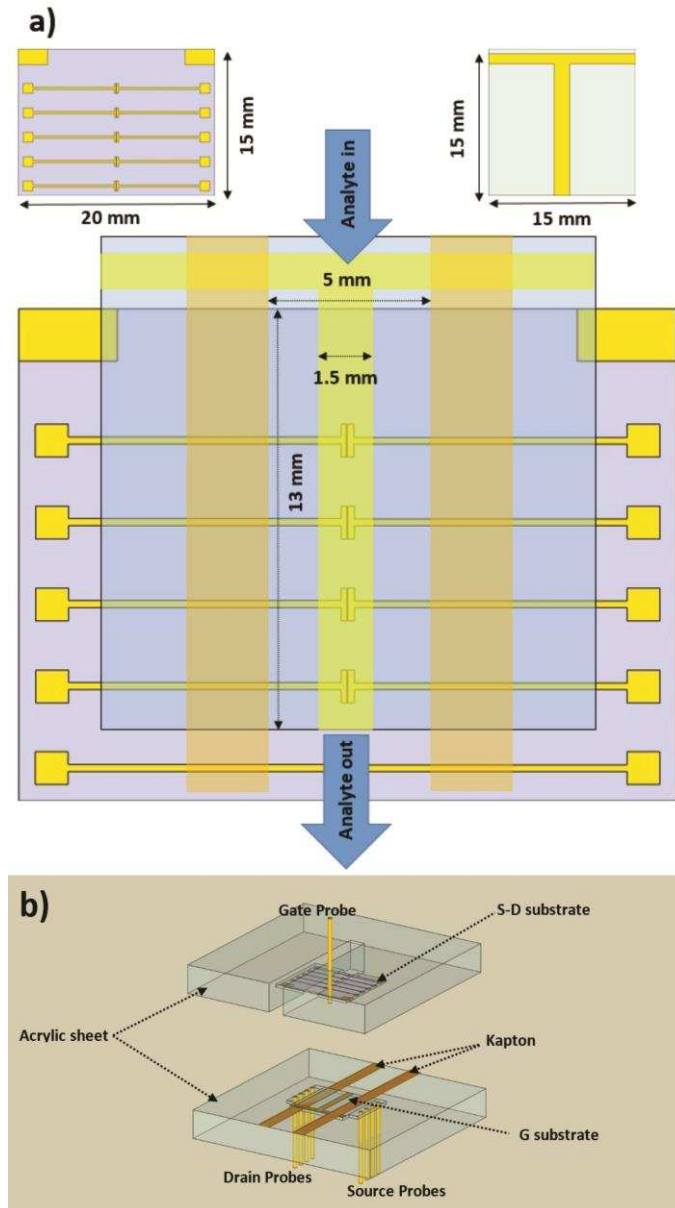
Fig. 1: PBTTT thin film transistors. **1a**: 'Sandwich' flow cell: Five Au source/drain contact pairs and T-shaped Au gate contact on separate substrates are mated face- to face with a Kapton spacer. **1b**: The flow cell is held together by acrylic sheets with machined recesses to hold substrates, and S, D and G are electrically contacted by Au needles.
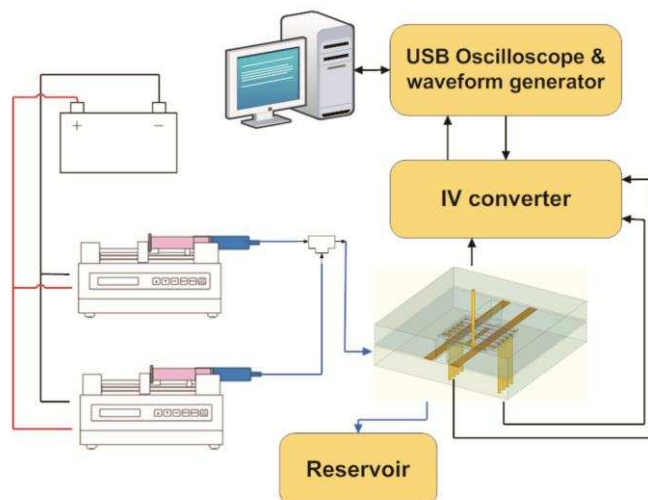
Fig. 2: Sketch of analyte delivery system for octylamine sensing.

Electrical characterisation: Flow cell OTFTs were linked to a real time electrical characterisation system wherein they are driven by a +/- 1V 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 $V_S = 1V$) *vs.* time; 'off current' (at $V_S = -1V$) was also recorded.

Results and Discussion

Fig. 3 shows the 'on- current' of a flow cell transistor under continuous pumping with plain DI water over *~2 hrs*. Data show low noise but OTFT peak drain current continuously drifts from an initially large negative value of 480nA at 1V source voltage towards lower values, approaching (147±10)nA that no longer drifts after 1 hr. 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.
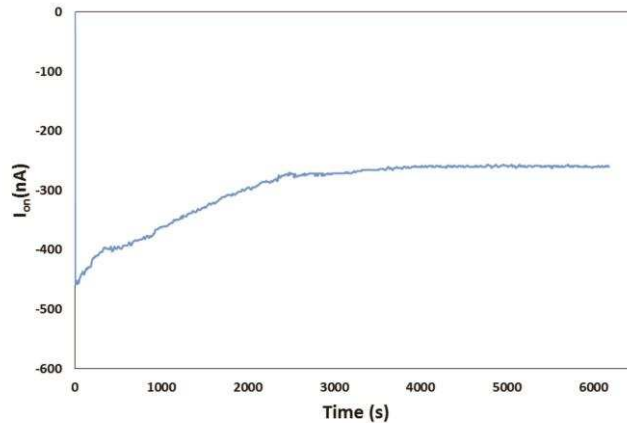
Fig 3: Response of water- gated PBTTT OTFT 'on' current under continuous pumping with plain DI water over *~2 hrs.*

Fig 4a shows a similar chart for a PBTTT OTFT that has previously been conditioned by < 1 hr 'washing' under continuous DI water purge. Now, octylamine analyte concentration is cycled between different levels with intermediate recovery periods under plain DI water purge. Time periods of exposure to analyte are shown shaded and are annotated with the respective concentration, recovery periods are clear. OTFT 'on' current rapidly drops to a reduced (less negative) level when the OTFT is exposed to octylamine solutions, and recovers under DI water purge over a period of ≈ 60 seconds (after low concentration octylamine exposure) up to ≈ 210 seconds (after exposure to higher octylamine concentration). As a control, we also exposed PBTTT OTFT to 1-octanol solutions, Fig. 4b. Despite the higher accessible maximum concentration (saturation at 3.53 *mM vs.* 1.54 *mM*), response is weak, does not systematically increase with increasing concentration, and is largely transient, occurring briefly after switching pump rate ratios, *cf.* Materials and methods / Analyte delivery. Within a few seconds after switching pump rates, I_{ON} settles back to approximately the prior value, regardless if the OTFT is now under DI purge, or under high 1-octanol concentration. PBTTT does not respond to water-borne alcohols in the same way it responds to amines.
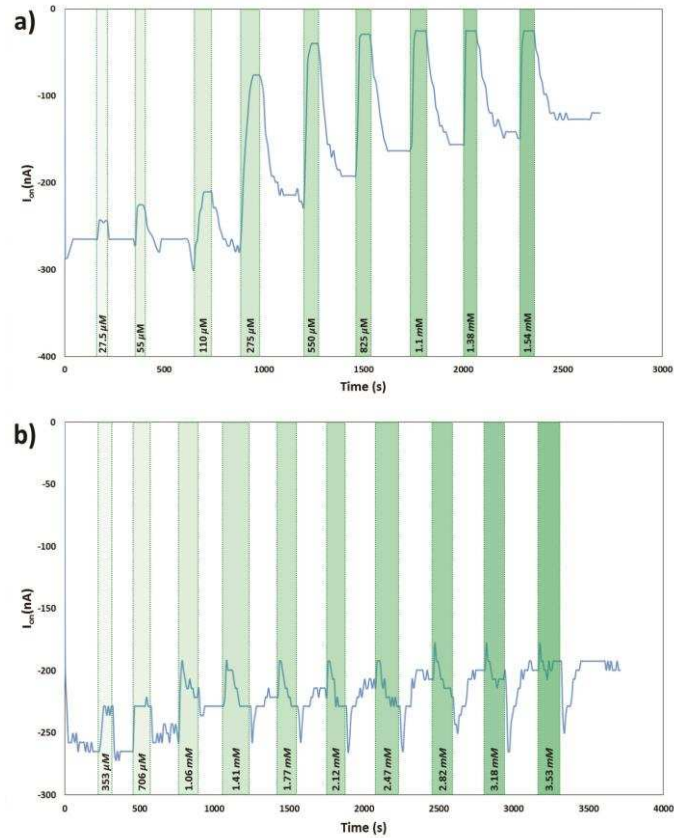
Fig 4a: Response of water- gated PBTTT OTFT 'on' current under exposure/recovery cycles to octylamine concentrations ranging from 27.5 to 1540 μM. **4b:** Control experiment with 1-octanol, concentration ranging from 353 μM to 3530 μM.

For quantitative analysis of the response of PBTTT OTFTs to water- borne amine, we exclude any effect of residual OTFT drift over time by normalising current response to analyte, $\Delta I_D(c)$, to $I_D(0,t)$, which stands for the drain current under purge immediately before analyte concentration c was applied. This results in the calibration chart for $\Delta I_D (c) / I_D(0,t)$, Fig 5a.
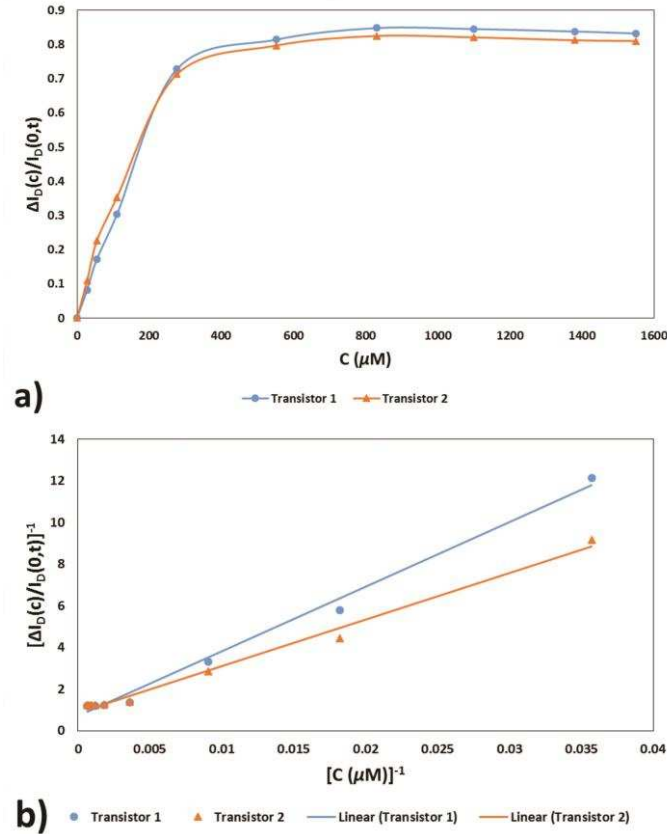
Fig 5a: Water- gated PBTTT OTFT on- current response to different octylamine concentrations in normalised form, $\Delta I_D(c) / I_D(0,t)$. Results are shown for two different transistors. **5b**: Same data plotted in the form $[\Delta I_D(c) / I_D(0,t)]^{-1}$ *vs*. c^{-1}.

Fig 5a shows data taken from two separate experimental series (similar as shown in Fig. 4) on different OTFTs, shown in different symbols. Both data sets fall on a very similar smooth curve, indicating a robust, repeatable calibration, independent from variation between transistor substrates. The drift of zero- analyte current with time is effectively compensated by both, prior conditioning, and normalising OTFT current response to amine to the zero- analyte current immediately before exposure. The calibration curve shows a steep rise at low concentrations, but levels off to a saturated response of ≈ 0.8 well before octylamine concentration in water saturates at 1540 μM. This shape resembles a Langmuir adsorption isotherm that predicts fractional monolayer coverage $\Theta(c)$ for mutually independent adsorption sites on a smooth solid surface in contact with a fluid carrying an adsorbate at concentration c:

(eq. 1) $\Theta(c) = kc / (1 + kc)$

Wherein k is a constant dependant on the strength of adsorbate/surface interactions, and temperature. $1/k$ corresponds to the concentration that leads to $\Theta = \frac{1}{2}$. If we identify octylamine analyte as the adsorbate and assume $[\Delta I_D(c) / I_D(0,t)]$ is proportional to $\Theta(c)$, this suggests a plot $[\Delta I_D(c) / I_D(0,t)]^{-1}$ *vs*. c^{-1} should result in a straight line with positive slope and positive intercept,

with the ratio of slope/intercept equal to *1/k*. Such a plot is shown in Fig. 5b, data at low concentrations (large c^{-1}) are fitted well by a straight line, albeit the small differences between the two transistors' original data are amplified, and data for high c (low c^{-1}) saturate, *i.e.* level off to a flat (zero slope) line. Overall the Langmuir isotherm gives a qualitatively reasonable fit to the observed *[$\Delta I_D(c)$ / $I_D(0,t)$] vs.* c data, which indicates adsorption of water-borne amine onto PBTTT surface, rather than bulk penetration. It is generally established that the Langmuir isotherm in its simple form, eq. 1, often only gives an approximate fit to experimental data, and modifications are required for quantitative analysis [19]. When *1/k* is nevertheless calculated from the fit parameters of the Langmuir plot Fig. 5b, we find 440 *μM* (transistor 1) / 250 *μM* (transistor 2), but relative error (in particular for intercept) is large. Inspection of the original data (Fig. 5a) suggests Θ = ½ (*i.e. $\Delta I_D(c)$ / $I_D(0,t)$* = 0.4) is reached for approximately 150 *μM* octylamine concentration for both transistors.

Conclusions

The innate sensitivity of organic semiconductors to amine vapours [2-9] translates to water-borne amines. We demonstrate this with the help of water- gated PBTTT OTFTs, which respond with a reduced drain current when octylamine is added to the gating water. Underlying OTFT drift is minimised by initial conditioning, and 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 reversible by purge in pure water. Sensor response can be approximated by a Langmuir adsorption isotherm. This suggests water-borne octylamine physisorbs from aqueous solution to adsorption sites at the PBTTT surface, rather than penetrating into PBTTT bulk, with a consequential reduction of OTFT current in proportion to fractional surface coverage due to the known de- doping effect that amines have on p- type organic semiconductors. Note that the accumulation layer in a water- gated OTFT forms at the same surface where analyte may adsorb, allowing an immediate influence of adsorbate on charge transport. In a control experiment, we find little response of PBTTT OTFTs to similar and higher concentrations of a different solute, 1-octanol, which apparently interacts far less strongly with PBTTT than the corresponding amine.

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