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Innate cation sensitivity in a semiconducting polymer

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Abstract

Water- gated organic thin film transistors (OTFTs) using the hole transporting semiconducting polymer, poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT), show an innate response of their threshold voltage to the addition of divalent metal cations to the gating water, without deliberately introducing an ion- sensitive component. A similar threshold response is shown for several divalent cations, but is absent for monovalent cations. Response is absent for transistors using the anorganic semiconductor ZnO, or the similar organic semiconductor poly(3-hexylthiophene) (rrP3HT), instead of PBTTT. We assign innate cation sensitivity to residues of the organometallic Pd(0) complex used as catalyst in PBTTT synthesis which bears strong resemblance to typical metal chelating agents. Organometallic Pd(0) residues are absent from ZnO, and also from rrP3HT which is polymerised with a different type of catalyst. However, when Pd(0) complex is deliberately added to rrP3HT casting solutions, resulting OTFTs also display threshold response to a divalent cation.

Introduction

The report by Berggren *et al.* [1] on the gating of thin film transistors (TFTs) using water as electrolytic gate medium marks the beginning of a new technology for the sensing of water-borne analytes, where the sample acts as an active part of the transducer. Since then a number of water- gated organic TFTs (OTFTs) have been demonstrated that respond selectively to water-borne analytes due to specific sensitisers that were introduced into the transistor architecture [2, 3]. This provides an alternative to the traditional ion- sensitive field effect transistor, which employs 'dry' (dielectric) gate insulators without direct contact between semiconductor and water-borne analyte [4]. Of particular interest to the present work is the report by List-Kratochvil *et al.* on a water- gated transistor that is sensitised for the selective detection of Na^+ ions with an ion- selective PVC membrane [5]. However, the design of List-Kratochvil *et al.* is rather sophisticated, employing a two compartment water cell (an analyte and a reference compartment), separated by the PVC membrane. The semiconductor is in direct contact with the reference compartment only, while the analyte compartment is addressed with an electrochemical reference electrode as gate contact.

Here we show that water- gated OTFTs using the organic semiconductor PBTTT poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene), Fig (1), originally synthesised by McCulloch *et al*. [6], show sensitivity to water-borne divalent cations, and selectivity between mono- and divalent cations, without further sensitising. Sensitivity and selectivity are innate to the semiconductor itself.

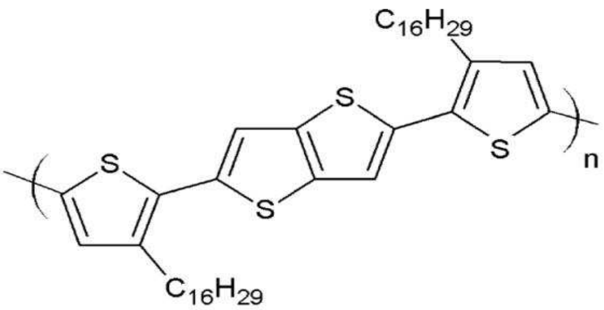

Fig (1): Chemical structures of semiconducting polymer PBTTT

Experimental

For TFT fabrication, synthetic quartz substrates, sourced from Ossila Ltd, were cleaned by acetone, isopropyl alcohol, and deionized water. 5 contact pairs per substrate of Gold (Au) source and drain contacts with a Chromium (Cr) adhesion layer were evaporated through a shadow mask with geometry width / length (W / L) = 1 mm / 30 µm = 33.3. PBTTT was sourced from Ossila Ltd, regioregular poly(3- hexylthiophene) (rrP3HT) from Aldrich; both were dissolved in 1,2 dichlorobenzene (DCB) at 7 mg/ml, filtered, and spin coated onto contact substrates from hot (100 ^{o}C) DCB for 40s at 5000 rpm. After casting, films were dried under dynamic vacuum at 180 ^{o}C for 30 min. For control experiments, anorganic semiconducting ZnO was prepared via thermal conversion of Zinc Acetate precursor cast from mixed ethanol/acetone; details in [7]. For another control experiment, rrP3HT solution was deliberately doped with 4% wt./wt. of the Pd(0) complex tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$], also sourced from Aldrich.

For cation sensing tests, we prepared 0.1M stock solutions of chloride salts of monovalent alkali metals Sodium (Na) and Potassium (K), divalent alkaline earth metals Calcium (Ca), Magnesium (Mg), Barium (Ba), and divalent transition metal Zn. Stock solutions were successively diluted 10- fold with DI water down to 1µM. 1 µL droplets of DI water and test solutions were applied as gate media to the channel region of PBTTT TFT substrates and electrically addressed by either Au (for organic semiconductor) or Tungsten (W) (for anorganic semiconductor) gate needles (American Probe and Technologies) bent into L-shape and held at fixed distance (~ 100µm) from the semiconductor surface using a probehead. Substrates were discarded after a single DI water / test solution / DI water test cycle to exclude biasing due to irreversible effects of prior exposure; gate needles were washed with DI water. We used a pair of Keithley source/measure units controlled by a LabVIEW routine to record linear transfer characteristics ((measurement of drain current I_D at drain voltage V_D = -0.1 V when gate voltage V_G was swept from zero to -0.6 V for PBTTT; voltage signs were reversed for ZnO) under ambient atmosphere. Threshold voltages V_{th} were extracted from linear transfer characteristics by linear extrapolation of drain current $I_D(V_G)$ curves to I_D = 0. Threshold change due to cation concentration c, $\Delta V_{th}(c)$, was taken as the difference between V_{th} under cation *vs*. V_{th} under DI water measured on the same substrate immediately before. We also evaluate the product of (linear) carrier mobility and specific gate capacitance, μC_i, from the slope of the linear transfer characteristic above threshold by eq. 1, based on standard TFT equations [8].

$$\mu C_i = \frac{L}{W} * \frac{1}{V_D} * \frac{\partial I_D}{\partial V_G} \qquad (1)$$

Results are reported in the form μC_i rather than μ itself because the specific capacitance of electrolyte solutions is not exactly known, and will vary with cation concentration.

Results and Discussion

We notice a significant difference in the response of water- gated PBTTT TFTs to mono- and divalent cations. While the response to monovalent cations (Na^+, K^+) is weak (see Fig. 4a below), PBTTT OTFTs respond strongly to divalent cations (Ca^{2+}, Mg^{2+}, Ba^{2+}, Zn^{2+}), without any sensitising. Fig. 2 shows linear transfer characteristics of water- gated PBTTT OTFTs gated with $CaCl_2$ solutions spanning five orders of magnitude in concentration (1 μM to 100 mM), each referenced to a linear transfer characteristic of same device under DI water. The 1μM Ca^{2+} linear transfer characteristic is near identical to the DI water transfer characteristic. However, for Ca^{2+} concentrations > 1μM, it is immediately obvious that increasing Ca^{2+} concentration leads to increased threshold, and reduced carrier mobility. This is a remarkable observation because we have not deliberately introduced any cation- sensitive component to the OTFT, like the PVC membrane in the work of List-Kratochvil *et al* [5]. The threshold shift is an innate property of the PBTTT OTFT itself. Nevertheless, we can sense Ca^{2+} with a similar limit- of- detection (LoD) of ~1μM as List-Kratochvil et al found for Na^+. We note that 'off' currents (I_D at reverse bias gate voltages) remain low even under high Ca^{2+} concentration, which speaks against bulk electrochemical doping, as in an electrochemical transistor.

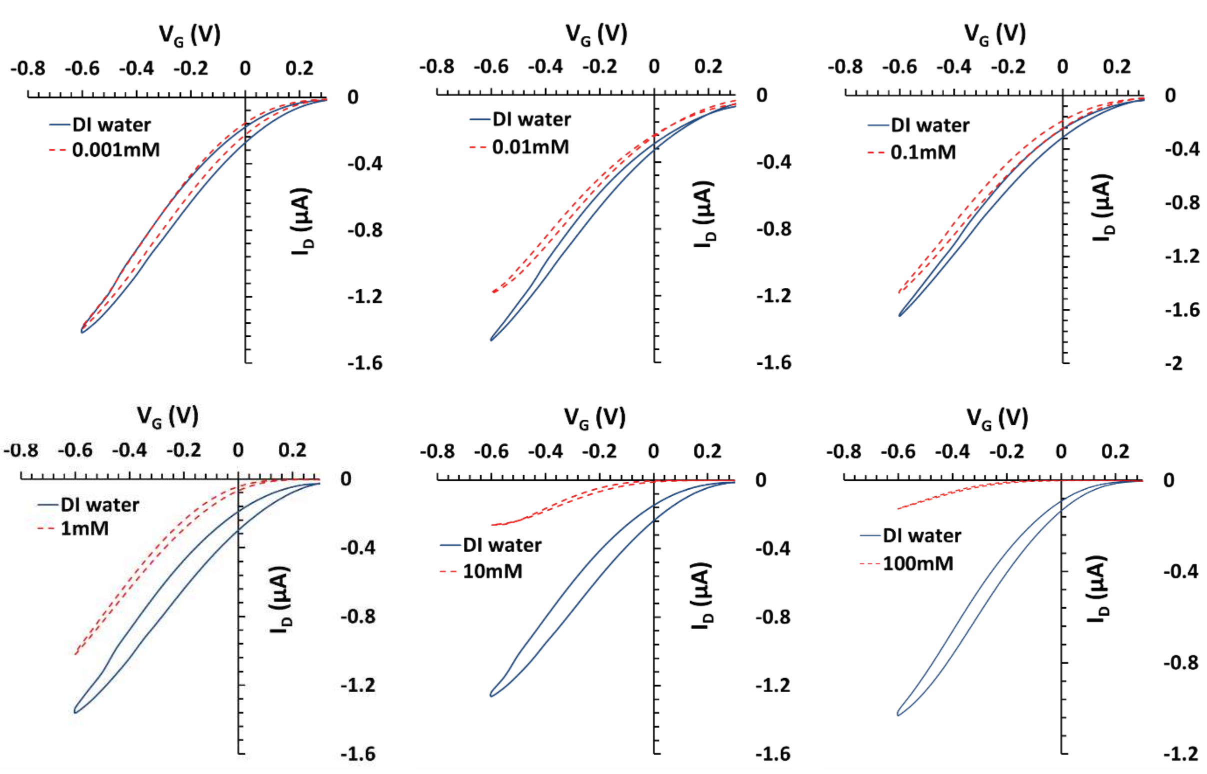

Fig. 2: Linear transfer characteristics of water- gated PBTTT OTFTs with different $CaCl_2$ concentrations (red), each referenced to same characteristic taken under DI water (blue) immediately before. Substrates were discarded after single use.

For quantitative analysis, we use the Nikolsky-Eisenman equation 2b [9], which is a refinement of the Nernst equation 2a [5].

$$\Delta V_{th} = s\Delta\log(a) \qquad (2a)$$

$$\Delta V_{th} = s\Delta\log(a + a_{st}) \qquad (2b)$$

Wherein slope s is given by 58/z mV/decade at T = 20 °C with z the valency of the detected ions, a is the ion's activity, and a_{st} is a constant characteristic of the respective cation-sensitive system. We here approximate activities by concentrations, c. For c >> c_{st}, eqn.s 2a and 2b are virtually identical. However, for small concentrations in the order c_{st} and below, the Nikolsky-Eisenman equation predicts a limit- of- detection (LoD) $c_{LoD} \sim c_{st}$, which is practically observed but is not reflected by the Nernst equation which unrealistically tends to $-\infty$ for $c \rightarrow 0$. We therefore first determine c_{st} by plotting observed ΔV_{th} data against log c (Fig. 3a), fit a straight line at high c, evaluate slope s, and find c_{st} as the point where results stand above the extrapolated high- c straight line by s log2 = 17 mV; this is implied by eq. 2b as the point where log c = log c_{st}. Fig. 3a gives c_{st} = 4.5 µM.

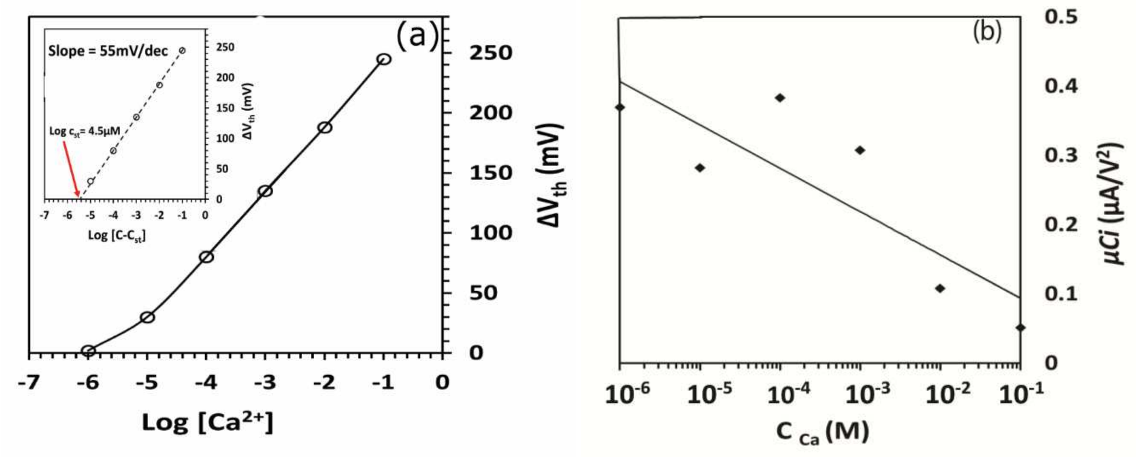

Fig. 3a,b: Threshold shift ΔV_{th} vs. log (c) scale (a) and vs. log (c-c_{st}) scale (inset to a, c_{st} = 4.5 µM). c_{st} = 4.5 µM is evaluated from 3a. Slope s in the inset is 55 mV/decade. 3(b): Product of carrier mobility and specific capacitance, μC_i, all for water- gated PBTTT OTFTs gated with $CaCl_2$ solutions of different concentrations.

We then plot same ΔV_{th} data against a log (c - c_{st}) scale, using c_{st} = 4.5 µM. This gives a near-perfect straight line with slope 55 mV/dec, inset to Fig. 3a. Remarkably, this is close to the slope 58 mV/dec for a single- valency ion (z = 1), rather than z = 2 as for Ca^{2+}. We will return to this point in the conclusions.

Fig 3b also shows a systematic decline of the product of carrier mobility and specific capacitance with increasing Ca^{2+} concentration, albeit we have no theoretical model for this shift. In the previous work on ion- sensitive water gated transistors by List-Kratochvil *et al.*

[5], only a threshold shift was observed in response to cation exposure, but no change of mobility. In the more sophisticated design of List-Kratochvil *et al*. [5] there is no direct contact between sample solution and semiconductor: The semiconductor remains in contact with a reference solution of fixed ion concentration. In our simpler transistor design, the analyte solution (of varying concentration) is in direct contact with the semiconductor. This direct contact may lead to a penetration of cations into the semiconductor and hence, an influence of cation concentration on mobility as well as threshold. Mobility and threshold therefore need to be disentangled for analysis, as we did here. After exposure to high Ca^{2+} concentrations, OTFTs did not recover to their initial behaviour under DI water gating, even after washing of the semiconductor film.

Following the remarkable observation of sensitivity to divalent cations in a water gated transistor without any deliberate sensitising, we have conducted a number of control experiments to investigate how specific, or general, this sensitivity is. Fig. 4 shows a comparison of water- gated PBTTT OTFTs exposed to a number of different cations dissolved in water, both mono- and divalent. We now only compare DI water and the highest cation concentration (100 mM) of the previous range.

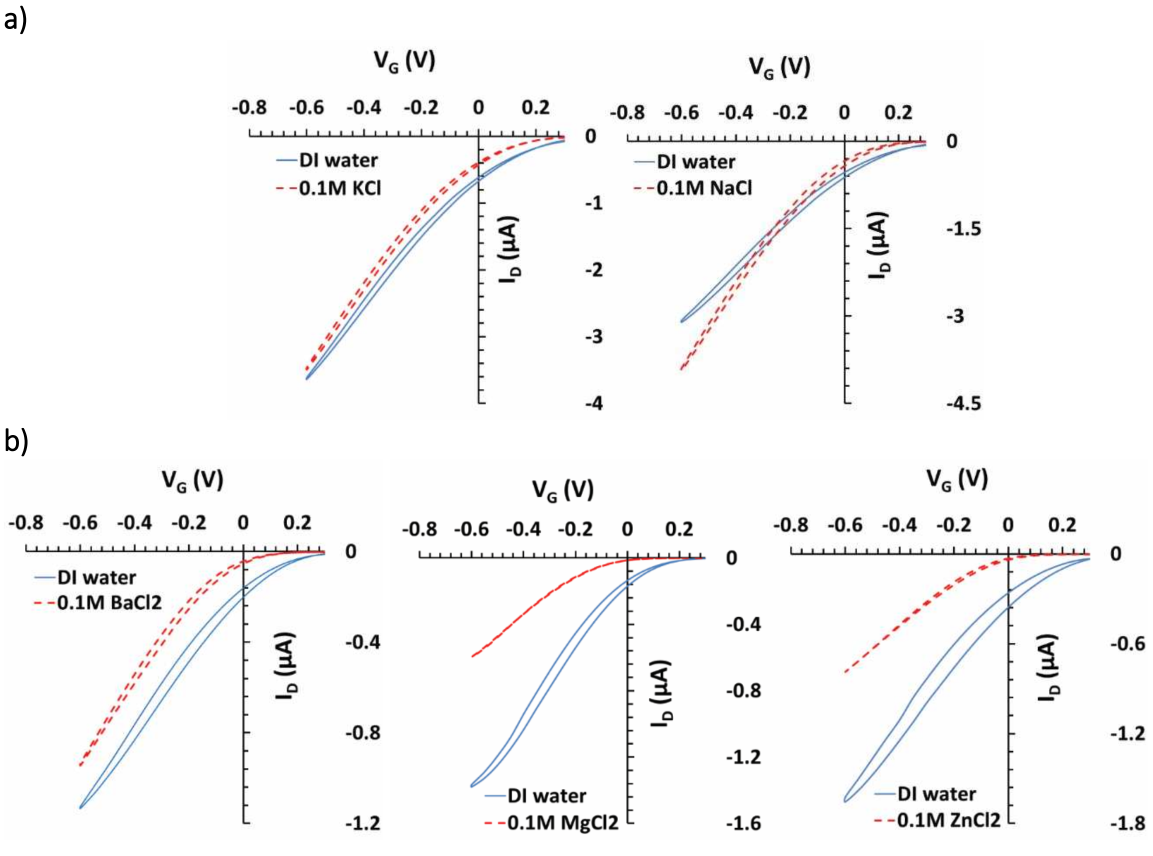

Fig 4: PBTTT OTFTs gated with solutions of various cations. **4a**: Monovalent cations (Na^+, K^+). **4b**: Divalent cations (Ba^{2+}, Mg^{2+}, Zn^{2+}). All OTFTs were electrically addressed with a Au gate needle.

We observe no threshold shift, and little change of slope (i.e. μC_i) in the linear transfer characteristic, in response to monovalent cations (Na^+, K^+), cf. Fig. 4a. However, we again find a significant threshold shift, and mobility decline, for 100mM *vs*. DI water for all divalent cations tested (Ba^{2+}, Mg^{2+}, Zn^{2+}), which is quantitatively similar to the response to Ca^{2+}. This shows that the threshold shift of unsensitised PBTTT OTFTs under cation exposure is tied to the bivalent character of the cations, albeit indifferent to their precise chemical character (alkaline earth *vs*. transition metal). The comparison between Na^+ and Ca^{2+} is particularly interesting, as both have very similar ionic radii (114 pm for Na^+ *vs.* 116 pm for Ca^{2+} [10]). Nevertheless, threshold response is observed for the bivalent ion only. On the other hand, the ionic radius of Mg^{2+} (86 pm) is significantly smaller than Ca^{2+} or Na^+, but the PBTTT OTFT response to Mg^{2+} is similar as to Ca^{2+}. It is thus the cation valency, not its size, that controls sensitivity.

In a further control experiment we compare the response of water- gated TFTs under exposure to Ca^{2+} cations when a different type of semiconductor is used in the TFT channel. As contrast to the hole transporting polymer semiconductor PBTTT, we used an anorganic, non- polymeric semiconductor, precursor- route ZnO. ZnO is an electron- transporting II-VI semiconductor which is known to work well under water- gating [7, 11]. Note that to date no water- gated electron transporting organic semiconductor is known, and solution processed (precursor- route or chemical bath deposited) II-VI semiconductors like ZnO or CdS lead to n-type TFTs even without doping as their valency bands lie too deep for efficient hole injection even from Au contacts. Hence comparison of PBTTT to n- type organic materials, or p- type solution processed anorganics, is impossible. Results are in Fig. 5:

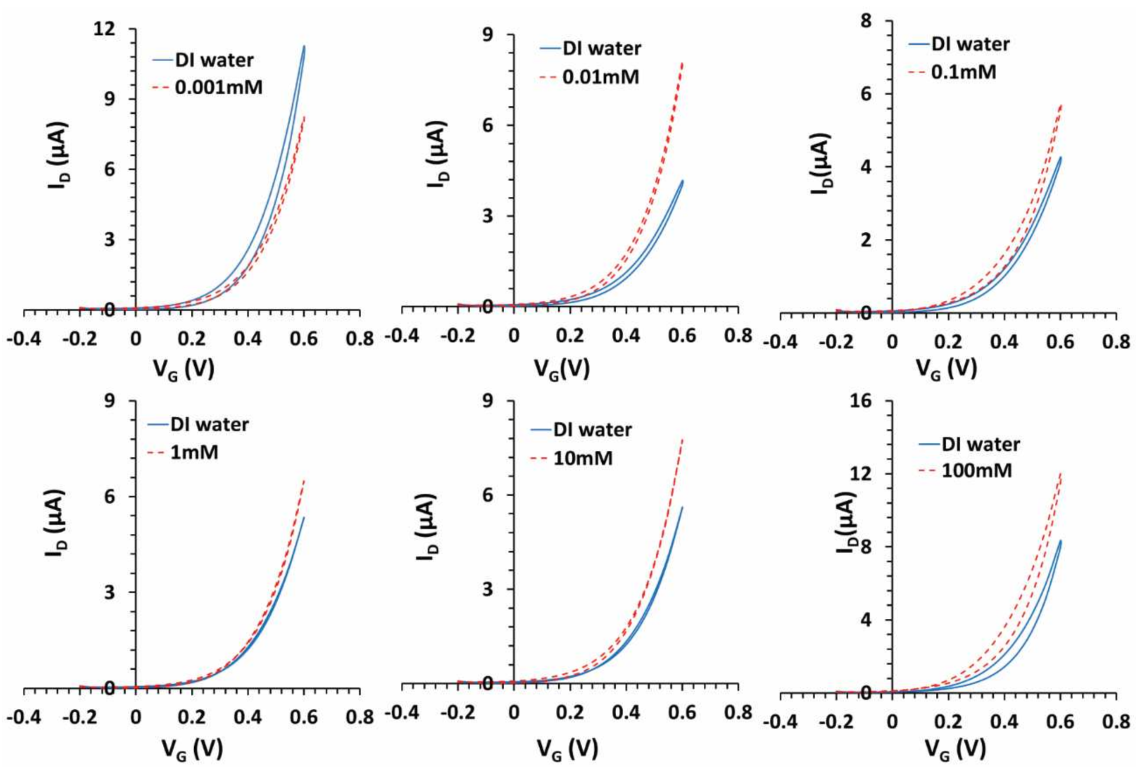

Fig. 5 Linear transfer characteristics of water- gated ZnO OTFTs with different $CaCl_2$ concentrations (red), each referenced to same characteristic taken under DI water (blue) immediately before. Fig. 5 is analogous to Fig. 2 but with a different semiconductor, ZnO vs. PBTTT.

Sign of voltages and current are reversed (now positive) due to the electron- rather than hole transporting character of ZnO vs. PBTTT. As expected, we observe good transistor performance of ZnO under water- gating. However, in contrast to PBTTT, we find no systematic threshold shift with Ca^{2+} concentration for water- gated ZnO TFTs, this is illustrated in Fig. 6.

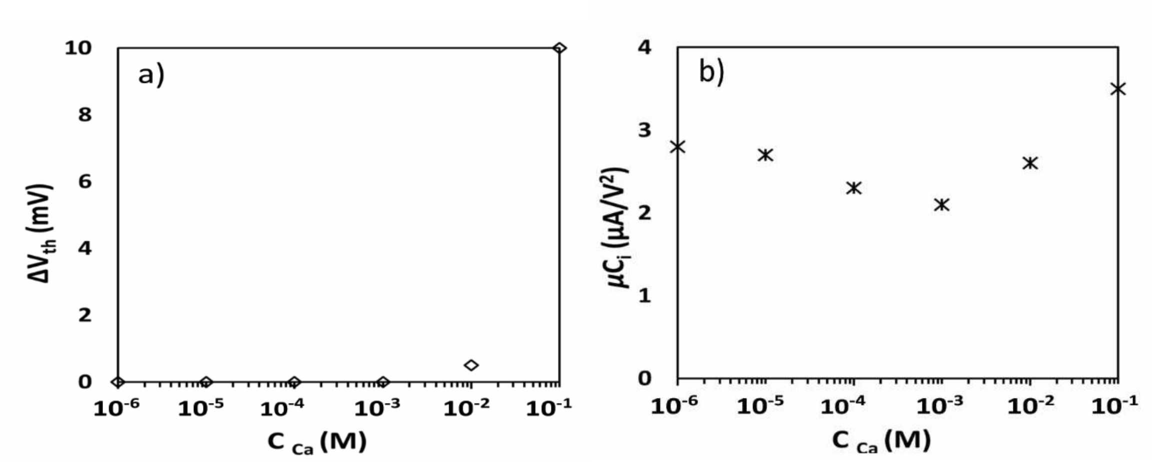

Fig. 6a,b Threshold shift (a) and the product of carrier mobility and specific capacitance μC_i (b) for water- gated ZnO OTFTs gated with $CaCl_2$ solutions of different concentrations against logarithmic concentration scales. Fig. 6 is analogous to Fig. 3 but with a different semiconductor, ZnO vs. PBTTT.

For ZnO TFTs, V_{th} does not depend on Ca^{2+} concentration up to 10mM, only at very high c (100mM) we find a small threshold shift (note the scale in Fig. 6a is expanded 25- fold compared to 3a), which may be related to the higher capacitance of concentrated salt solutions rather than a Nernstian threshold shift due to semiconductor- cation interactions. Similarly, μC_i shows only weak and irregular variation with Ca^{2+} concentration, not the systematic drop as for PBTTT OTFTs, Fig. 3b. In similar experiments (not shown here) with Na^+, K^+, Ba^{2+}, Mg^{2+}, and Zn^{2+} cations, we again find no significant threshold shift for water- gated ZnO TFTs. The sensitivity to divalent ions observed for the organic semiconductor PBTTT is absent in water- gated ZnO TFTs.

As a final control experiment, we have also tested the widely studied hole transporting semiconducting polymer rrP3HT for response to divalent cations, Fig. 7.

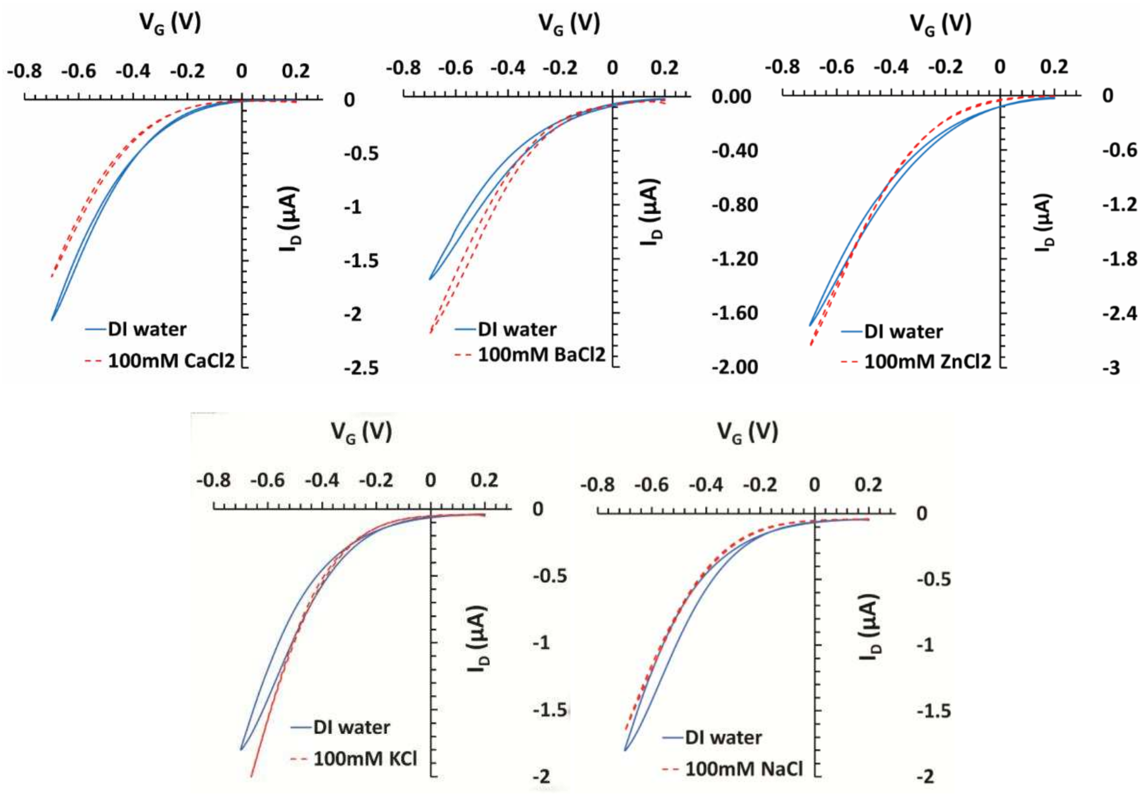

Fig. 7: Linear transfer characteristics of P3HT OTFTs gated with solutions of (Ca^{2+}, Ba^{2+}, Zn^{2+}, K^{+}, and Na^{+}) (red), referenced to same characteristic taken under DI water (blue) immediately before. OTFTs were electrically addressed with an Au gate needle.

Fig. 7 shows only a small threshold shift even under 100 mM Ca ion vs. DI water, whereas Ba, Zn, K, and Na ions vs. DI water show no threshold shift. Although both rrP3HT and PBTTT are based on thiophene, the innate sensitivity to divalent cations observed for PBTTT is absent in rrP3HT.

Conclusions

We find that water- gated OTFTs using the hole transporting semiconducting polymer PBTTT show sensitivity of their threshold voltage to the addition of divalent metal cations to the gating water. This is an innate property of the PBTTT semiconductor, without deliberately introducing an ion- sensitive component to the transistor. In a number of control experiments, we clearly establish the link of the observed sensitivity specifically to the interaction between semiconductor PBTTT, and divalent cations. We observe no similar response of water gated PBTTT transistors to monovalent cations. It is also absent when an inorganic semiconductor (ZnO) or a different semiconducting polymer (rrP3HT) is used.

We assign the observed innate sensitivity to catalyst residues remaining from the Stille coupling used in the synthesis of PBTTT. Stille coupling is catalysed by the organometallic Pd(0) complex tris(dibenzylideneacetone)dipalladium(0), $Pd_2(dba)_3$ [6]. Sensitisers used in PVC membranes typically also are organic metal- complexing agents at low concentration [12, 13], including the membrane used by List-Kratochvil et al. [5] which is described in [14]. The ability of alkaline earth metals to form organometallic complexes is established [15], they may therefore compete with Pd for complexation with tris(dibenzylideneacetone). ZnO, in contrast, is impermeable and does not contain catalyst residue. Our interpretation is ~~further~~ supported by the lack of strong divalent cation sensitivity in rrP3HT. Albeit chemically similar to PBTTT, rrP3HT polymerisation is catalysed by Rieke Zinc [16] rather than $Pd_2(dba)_3$. This introduces no organometallic residue into P3HT. To support this interpretation further, we have deliberately added 4% wt./wt. Pd2(dba)3 to rrP3HT casting solution. We find that the resulting $Pd_2(dba)_3$- doped rrP3HT OTFT displays strong threshold shift to 100 mM Ca^{2+} (Fig. 8), similar as PBTTT OTFTs in Fig. 2, while undoped rrP3HT OTFTs not (Fig. 7). This confirms that $Pd_2(dba)_3$ introduces sensitivity to divalent cations when present in a semiconducting polymer.

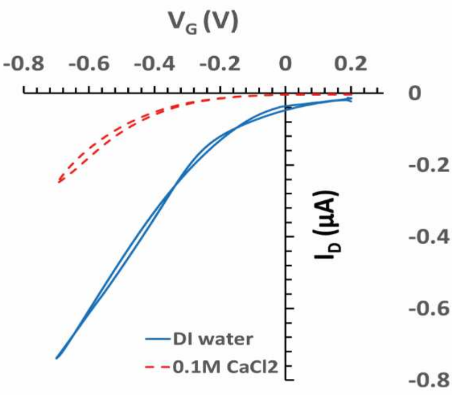

Fig. 8 Linear transfer characteristics of rrP3HT OTFTs when rrP3HT casting solution was deliberately doped with Pd(0) catalyst, $Pd_2(dba)_3$. Gating was with DI water (blue, solid line), and 100 mM $CaCl_2$ solution (red dashes). OTFTs were electrically addressed with an Au gate needle.

Remarkably, PBTTT OTFT threshold voltage shifts with 55 mV/decade in response to divalent cations, almost exactly the value expected for monovalent cations, albeit PBTTT sensitivity is for divalent ions only. Speculatively, this may be because a single divalent cation replaces both Pd(0) in $Pd_2(dba)_3$, which go into solution as 2 Pd^+:

$$Ca^{2+}_{aq} + Pd_2(dba)_3 \rightarrow Ca(dba)_3 + 2Pd^{+}_{aq}$$

The release of two Pd^+ for every complexed Ca^{2+} would cancel the division by z = 2 of s in eq. 2b, and Pd(I) is a possible Pd oxidation state. However, we have no proof for this mechanism.

Practically, our observations may be used to detect the presence or arrival of divalent ions against a background of monovalent ions, even when the latter are much more concentrated than the former, with a generic OTFT design. PBTTT- based bivalent cation sensitive OTFTs require no electrochemical reference electrode, and no ion- specific PVC membrane, to perform their function. On the other hand, the innate sensitivity of PBTTT to divalent cations must be taken into account in future water gated OTFT- based sensor designs. Divalent cations will act as interferants that must be accounted for. A simple way to avoid such interference is the use of rrP3HT instead of PBTTT.

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