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# A membrane- free cation selective water- gated transistor

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## Abstract

Sensors for the detection of waterborne cations are of great practical interest, and chemistry has synthesised a formidable catalogue of cation selective complexation agents ('ionophores') as selective sensitisers (e.g. <sup>9-13, 15-19, 28, 29</sup>). Current ionophore- based sensors separate the complexation of the cation by the ionophore, and the transduction of complexation into an electrical signal, into separate components. We here unite both functions into a single, sensitised semiconducting layer of a water- gated organic thin film transistor (OTFT). The resulting OTFT transduces waterborne cations into an electrical signal with same selectivity, sensitivity, and limit of detection as established sensors at much simplified preparation and operation. This opens a new route to apply the 'ionophore' family of functional organic materials in practical cation sensors.

## Introduction

Dissolved cations are ubiquitous in natural water, and may either represent valuable micronutrients ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , ...), or deadly poisons ( $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , ...) <sup>1, 2</sup>. Consequently, a number of sensitive techniques, e.g. atomic absorption spectroscopy <sup>3</sup>, atomic emission spectroscopy <sup>4, 5</sup> and mass spectroscopy <sup>6</sup> have been developed to detect waterborne cations at low concentrations. However, these techniques require expensive instrumentation and infrastructure that is not easily portable to the point of need <sup>7</sup>.

As a lower cost, more portable alternative, organic chemistry has developed organic metal complexing agents as sensitisers that bind to waterborne cations, these are known as 'ionophores'. A classical example is 1-(2-pyridylazo)-2-naphthol (PAN) <sup>8</sup>, which (rather unselectively) chelates many bivalent cations. More recently a range of macrocycles

(calixarenes<sup>9, 10</sup>, porphyrines<sup>11</sup>, phthalocyanines<sup>12, 13</sup>), and conjugated polymers bearing crown ether ligands<sup>14</sup>, have been reported with sometimes highly selective complexing of metal cations in their central cavity. Most important cations now have 'their' selective macrocycle. Sometimes ionophores can be transduced by 'colorimetry' as cation complexation may lead to a change of optical absorbance. Often, complexation is instead transduced electrochemically [e.g.<sup>15</sup>] via a change in interfacial potential. However, many macrocycles are almost insoluble in water<sup>16,17</sup>. For application to aqueous media, the contact between insoluble sensitizer and waterborne cations is usually mediated by embedding sensitizers in plasticised PVC membranes<sup>15, 18, 19</sup>; a theoretical treatment is in<sup>20</sup>.

The discovery of Berggren *et al.*<sup>21</sup> that water can act as an electrolytic gate medium for thin film transistors (TFTs) has paved the way for novel 'electrophysical' rather than electrochemical transducers for waterborne analytes, as transistor threshold voltage is sensitive to interfacial potentials. Water-gated TFTs that incorporate suitable sensitizers therefore display a shift of transistor threshold voltage in response to waterborne analytes, e.g.<sup>22</sup>. Sensitized PVC membranes have since been introduced into water-gated TFTs that consequently acted as cation-selective sensors<sup>23, 24</sup>.

On the example of calcium, we here demonstrate a simplified OTFT architecture for selective detection of waterborne cations that requires no PVC membrane, and no electrochemical reference electrode as in previous reports<sup>23, 24</sup>. We deliberately add a small amount (1% wt./wt. of rrP3HT) of a calcium-selective calix[4]arene, 'calcium ionophore VI'<sup>25</sup> as a sensitizer to rrP3HT spincoating solution. We find that water-gated OTFTs cast from sensitized rrP3HT solutions selectively respond to calcium cations dissolved in the gating water in a very similar way to PVC membrane sensitized devices. This approach can easily be generalised to other cation-selective macrocycles.

## Experimental section

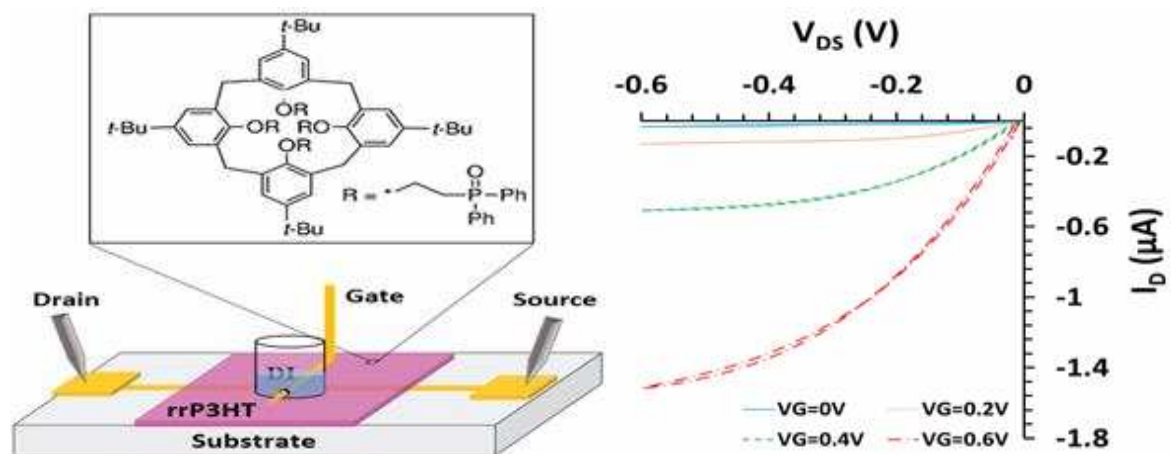
We fabricated transistor substrates on 20 mm x 15 mm flat glass slides coated with 20 nm of SiO<sub>2</sub>, sourced from Ossila Ltd, similar as described previously<sup>26,27</sup>. Glass / SiO<sub>2</sub> substrates were cleaned with solvents in an ultrasonic bath, and then in an UV ozone cleaner. We used

an Edwards high vacuum evaporator to deposit first a 20 nm Cr adhesion layer, then 120 nm Au contacts, onto substrates. Source/drain contact pairs were defined by an Ossila shadow mask (Ossila Order Code E291) which defines 5 source/drain contact pairs per substrate with geometry width / length ( $W/L$ ) = 1mm / 30 $\mu$ m = 33. The mask also defines a narrow track linking each contact to a distant 2 mm x 2 mm contact pad. We dropped Au needles onto the contact pads using Karl Suss probeheads to link to a Keithley source/measure unit. As semiconductor we purchased regioregular poly (3-hexyl thiophene-2,5-diyl) (rrP3HT) from Aldrich (Cat. No. 698989, electronic grade 99.995 % trace metal basis), dissolved 10 mg/ml in 1,2 dichlorobenzene (DCB) at 65 °C and filtered with 0.45  $\mu$ m polytetrafluoroethylene syringe filter. For sensitised transistors, we added 0.1 mg/mL (1% wt./wt. of rrP3HT) 'Calcium ionophore VI' sourced from Sigma Aldrich (Cat. No. 72385) to the same casting solution. Calcium ionophore VI is a calix[4]arene macrocycle (*cf.* Fig. 1) that selectively complexes  $Ca^{2+}$  in its central cavity, as described by McKittrick *et al.*<sup>25</sup> who used it with a PVC membrane based electrochemical transducer to sense waterborne  $Ca^{2+}$ . For control samples, rrP3HT was not sensitised. TFT substrates were completed by spin casting onto contact substrates for 60s at 2000 rpm. After casting, films were dried under dynamic vacuum at 110 °C for 40 min.  $CaCl_2$ , KCl, NaCl, and  $BaCl_2$  stock solutions were prepared at 0.1 M concentration in deionised (DI) water.  $CaCl_2$  stock solution was subsequently repeatedly diluted 10- fold down to 1  $\mu$ M. Transistor substrates were covered with PTFE films that had small 'windows' cut into them to expose individual source / drain contact pairs with intermediate transistor channel. A small plastic pool of 50  $\mu$ L capacity was mounted over the window and first filled with DI water for a reference measurement. The pool was then repeatedly emptied and filled again with  $CaCl_2$  solutions ranging from 1  $\mu$ M  $\rightarrow$  100 mM in ascending order. Fresh OTFT substrates were used for similar tests on  $BaCl_2$ , KCl, NaCl, but with DI water and 0.1M concentration only. TFTs were electrically addressed by an Au gate needle (American Probe and Technologies) bent into L- shape touching the surface of the aqueous gate medium. We did not use an electrochemical reference electrode. Our setup is illustrated in Fig. 1. OTFT transfer characteristics were recorded by sweeping gate voltage  $V_G$  from 0.2 to -0.7 V and back to 0.2 V in steps of 0.02 V at fixed drain voltage  $V_D = -0.3$  V. After each gate voltage step we allowed 2s for equilibration before recording drain current  $I_D(V_G)$ . We found negligible hysteresis between  $V_G$  ramping directions. Gate needles were washed with DI water after each measurement. To find threshold voltage shift  $\Delta V_{th}$  between

DI water- and sample solution- gated OTFTs, we plotted DI water gated and sample gated transfer characteristics in the same graph and shifted the sample- gated characteristics horizontally along the  $V_G$  axis to find the best possible overlap to the DI gated characteristic.  $\Delta V_{th}$  is the shift required for best overlap, the procedure is illustrated in Fig. 2c. Same procedure was used by Biscarini *et al*<sup>22</sup> for a water- gated dopamine- sensing OTFT. The described method does not assume a specific mathematical form for the  $I_D(V_G)$  characteristic which makes it most appropriate for the current situation, as our transfer characteristics are neither strictly linear nor saturated.

## Results and discussion

Fig. 1a illustrates of a sensitised water- gated OTFT setup we are using for the detection of waterborne  $Ca^{2+}$ , details of preparation are given in the experimental section.

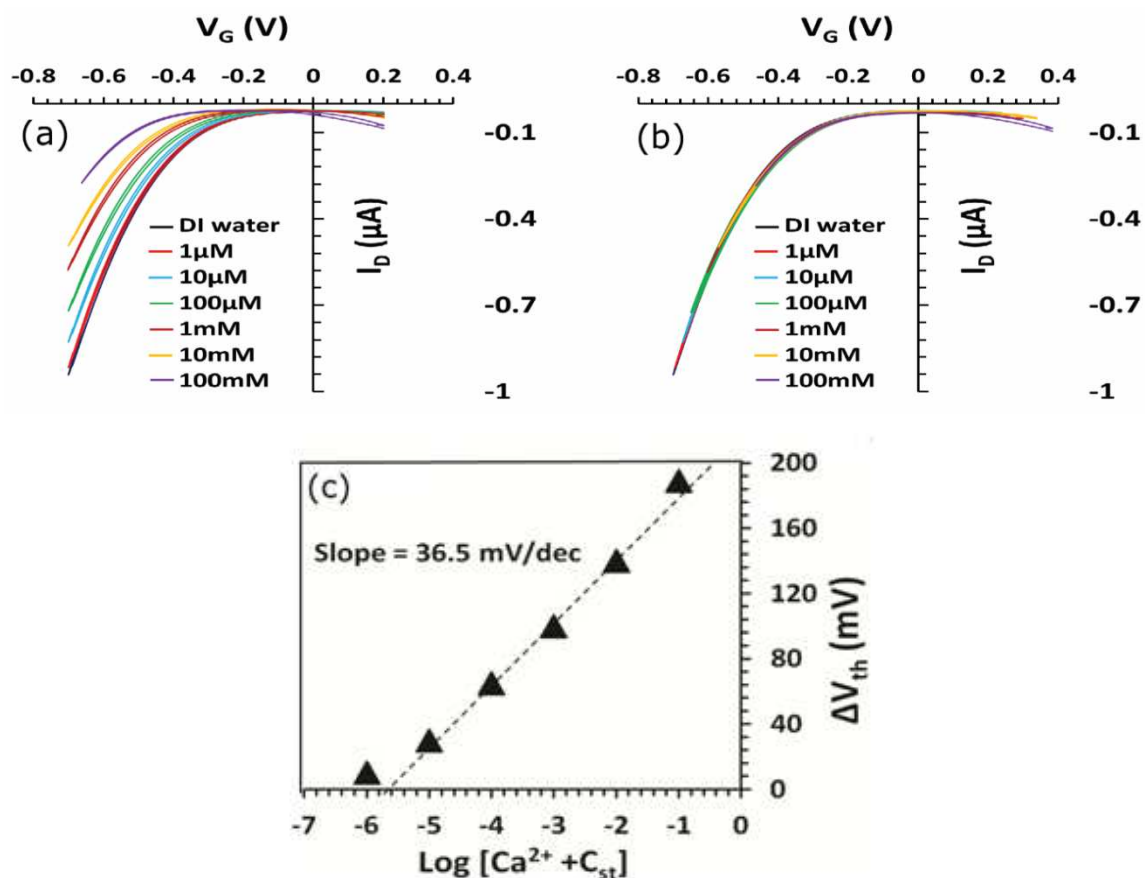


**Fig. 1(a)** Design of our  $Ca^{2+}$  sensitive water- gated OTFT. The semiconducting rrP3HT film is doped with 1% wt./wt of 'calcium ionophore VI', the ionophore's molecular structure is shown in the inset.. **(b)** Output characteristics of DI water gated OTFT sensor devices.

Note the similarity of this setup to a generic water- gated OTFT (e.g.<sup>21</sup>), the only added feature is the presence of 1% wt./wt. of calcium ionophore VI in the semiconducting film. We require no separate PVC membrane, and no electrochemical reference electrode. Fig. 1b shows an output characteristic for the OTFT in 1a. The characteristic is close to ideal, with very little hysteresis and low threshold ( $\approx 0.2$  V). Assuming a specific gate capacitance of  $3 \mu F/cm^{221}$  we estimate a carrier mobility of  $\approx 0.2$   $cm^2/Vs$  for a water-gated P3HT : 1% ionophore film. Doping with 1% ionophore does not compromise the use of P3HT films in

water- gated OTFTs, but it selectively sensitises them for the detection of  $\text{Ca}^{2+}$  ions added to the gating water, as we show in the following.

Fig. 2a shows the recorded transfer characteristics for ‘Calcium ionophore VI’ sensitised rrP3HT TFTs under DI water, and under  $\text{CaCl}_2$  solutions of increasing concentrations from  $1\mu\text{M}$  to  $100\text{mM}$  in factors of ten, all taken on the same OTFT substrate. Fig. 2a clearly shows an increase of threshold  $\Delta V_{\text{th}}$  with increasing  $\text{Ca}^{2+}$  concentration. This is quantified by the ‘master curve’ Fig. 2b, which shows all transfer characteristics shifted along the  $V_G$  axis for best overlap with the DI water characteristic. Note the excellent overlap of all curves, which shows that only threshold is affected by  $\text{Ca}^{2+}$ , carrier mobility is not. The  $V_G$  shift required for best overlap is identified as threshold shift,  $\Delta V_{\text{th}}$ , and is plotted in Fig. 2c against a logarithmic concentration scale.



**Fig 2.** (a) Transfer characteristics of rrP3HT: 1% Calcium ionophore VI OTFTs gated with different concentrations of  $\text{CaCl}_2$  aqueous solutions. Dark blue: DI water, coloured graphs for increasing concentration from  $1\mu\text{M} \rightarrow 100\text{mM}$  in factors of 10. (b) Same characteristics shifted along the  $V_G$  axis for best overlap with DI water gated transfer characteristic.  $\Delta V_{\text{th}}$  was taken as the  $V_G$  shift required for best overlap. (c) Threshold shift  $\Delta V_{\text{th}}$  plotted against  $\text{log} (c_{\text{Ca}} + 3.7\mu\text{M})$ , according to eq. 1b.

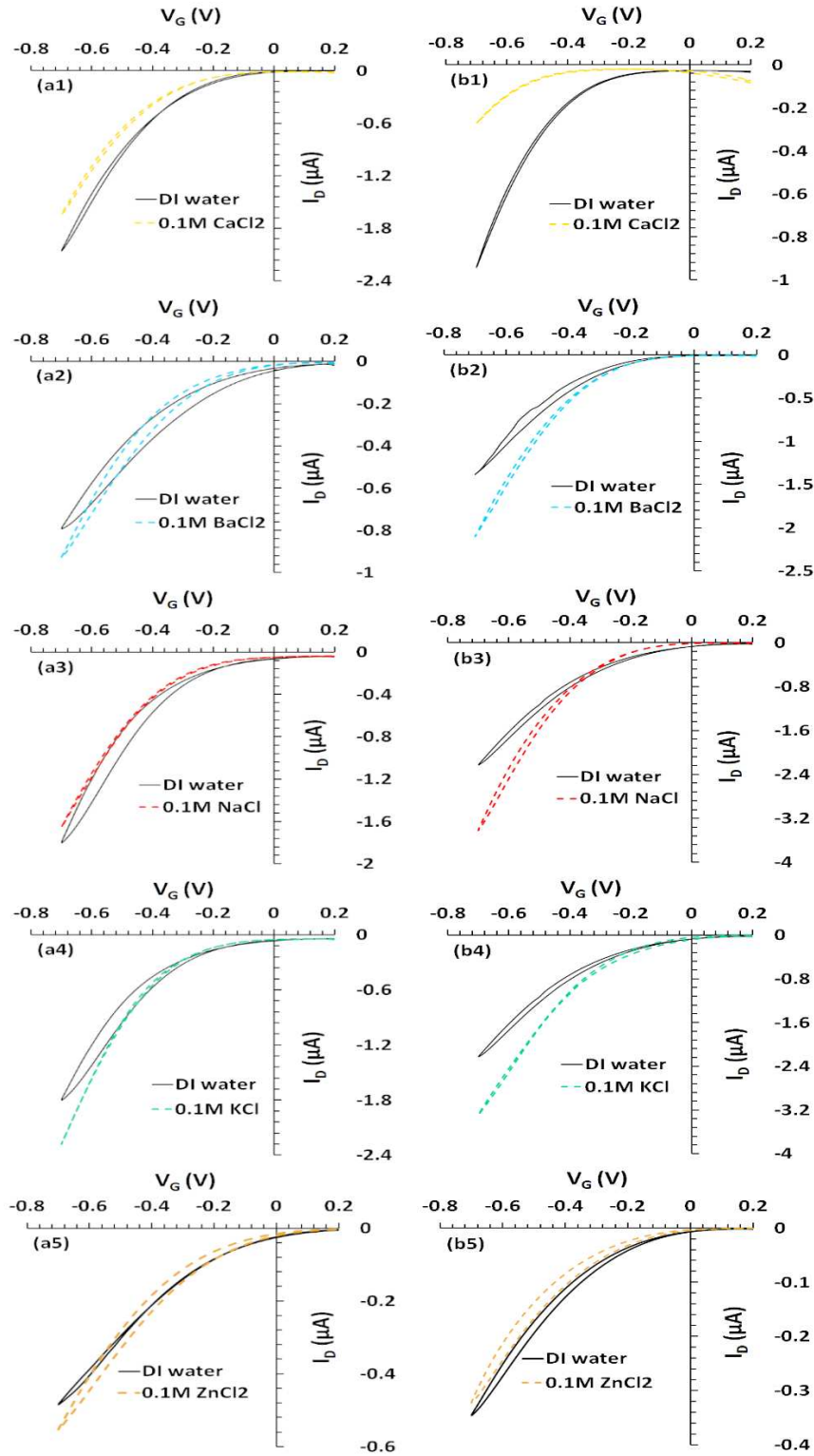
For quantitative analysis, we use a refinement of the Nernst equation 1a [e.g.<sup>15, 23-25</sup>], known as the Nikolsky-Eisenman equation 1b<sup>28</sup>:

$$\Delta V_{th} = s \Delta \log(a) \quad (1a)$$

$$\Delta V_{th} = s \Delta \log(a + a_{st}) \quad (1b)$$

Wherein slope  $s$  is given by  $58/z$  mV/decade at  $T = 20^\circ\text{C}$  with  $z$  the valency of the detected ions, here  $z = 2$  and  $s = 29$  mV/decade;  $a$  is the ion's activity, and  $a_{st}$  is a constant characteristic of the respective cation-sensitive system. Note, according to eq. 1, threshold shift is independent of ionophore concentration, hence no attempt was made to optimise it here, or elsewhere<sup>15,23-25</sup>. Ion activities ( $a$ ) in eq. 1 are here approximated by ion concentrations,  $c$ . For  $c \gg c_{st}$ , eqn.s 1a and 1b 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  $c \rightarrow 0$ . To estimate  $c_{st}$ , we used the following extrapolation: We plot observed  $\Delta V_{th}$  data against  $\log c$  and fit a straight line at high  $c$ , finding its slope  $s$ . We extrapolate that line to low  $c$  and identify the concentration where measured data stand above the extrapolated line by  $s \log 2$ . According to eq. 1b, this concentration equals  $c_{st}$ . We here find  $c_{st} = 3.7 \mu\text{M} \sim c_{LoD}$ , and finally plot  $\Delta V_{th}$  vs.  $\log(c + 3.7 \mu\text{M})$ , Fig. 2c. This gives a good straight line fit with slope  $s = 36.5$  mV/decade. PVC membrane sensitised water gated transistors also display a limit-of-detection in the order  $(1...10 \mu\text{M})$ <sup>23, 24</sup>, for some electrochemical transducers it may be somewhat lower (e.g.  $0.04 \mu\text{M}$  in<sup>15</sup>). When McKittrick et al transduced the same ionophore by traditional membrane potentiometry<sup>25</sup>, they did not explicitly quote a LoD, but Fig. 1 in [25] suggests a similar value as we find here.

We followed up with a series of control experiment to show that the result in Fig. 2 is indeed caused by sensitising rrP3HT with calcium ionophore VI, and that our transistors are selective to the 'target' analyte  $\text{Ca}^{2+}$  over other waterborne cations. We now only compare OTFTs gated with concentrated (0.1M) cation solutions vs. DI water gating.



**Fig. 3:** Response of P3HT transistors (a) without and (b) with 1% 'Calcium ionophore VI' sensitizer to 0.1M NaCl, 0.1M KCl, 0.1M BaCl<sub>2</sub> and 0.1M CaCl<sub>2</sub>. The selective sensitizer imparts sensitivity to Ca<sup>2+</sup> (b1) but not to Ba<sup>2+</sup> (b2). Response of P3HT transistors with and without 1% 'Calcium Ionophore VI' calix[4]arene sensitizer to 0.1M NaCl (a3, b3), KCl (a4, b4), and ZnCl<sub>2</sub> (a5, b5). Sensitised transistors show little threshold response to 0.1M Na<sup>+</sup>, K<sup>+</sup>, and Zn<sup>2+</sup>.



Fig. 3 (a1 and b1) compares an unsensitised to a sensitised P3HT TFT, both gated with 0.1M  $\text{CaCl}_2$ , both in comparison to DI water as gate medium. While the sensitised transistor (b1) shows a strong response to 0.1M  $\text{CaCl}_2$  (as it did in Fig. 2a), the unsensitised transistor's transfer characteristic (a1) is very similar under DI water and 0.1M  $\text{CaCl}_2$ . This confirms that rrP3HT shows no innate sensitivity to bivalent cations. Sensitivity to calcium is indeed introduced by the addition of 'calcium ionophore VI' to the casting solution. Fig. 3 (a2 and b2) compares the response of unsensitised and sensitised rrP3HT transistors to another bivalent earth alkali cation, 0.1M  $\text{BaCl}_2$ . Now, both characteristics are similar to each other, and to the DI water gated characteristic. This confirms that 'calcium ionophore VI' is selective to calcium, and imparts no barium sensitivity. Similarly, Figs 3 (a 3 and 4) and (b 3 and 4) compare the response of unsensitised and sensitised rrP3HT TFTs to 0.1M sodium and potassium, respectively. Again, the response to a cation concentration as high as 0.1M is very small even for the sensitised transistor (b 3 and 4), and in the opposite direction than for  $\text{Ca}^{2+}$ . In addition, McKittrick et al. [25] have already established  $\text{Ca}^{2+}$  selectivity of same ionophore over  $\text{Li}^+$ ,  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$  using traditional membrane- based potentiometry and there is very little response for unsensitised OTFTs ( a 3 and 4). A sensitised transistor also shows little response to 0.1M transition metal,  $\text{Zn}^{2+}$ , Fig. 3b 5. To summarise the control experiments, unsensitised rrP3HT transistors do not respond much to any cations in the gating water. rrP3HT transistors sensitised with 1% 'calcium ionophore VI' selectively respond to  $\text{Ca}^{2+}$  ions in the gating water with a threshold shift, but not to other similar ions.

## Conclusions

Electrical detection of waterborne cations with insoluble ionophores relies in two processes: The complexation of the cation by the ionophore, and the transduction of complexation into an electrical signal via the associated shift of interfacial potential. Established sensors split these processes over two separate functional components: Typically, a sensitised PVC membrane for cation/ionophore complexation, and an electrochemical transducer [e.g.<sup>15</sup>], or a TFT<sup>23, 24</sup>, to detect potential shift. We here unite both functions in a single layer that is deposited in a single step. We add a cation- selective ionophore to the casting solution of a semiconducting polymer before processing into a water- gated TFT. The resulting TFT detects and transduces waterborne cations without loss of selectivity, sensitivity, or limit of

detection, but with much simplified device preparation. We no longer require the PVC membrane, nor an electrochemical reference electrode. This opens a new, simple route to apply the formidable back catalogue of cation selective, water insoluble macrocycles (e.g.<sup>9-13, 15-19, 29, 30</sup>) for practical cation sensors.

We suggest two lines of future work. Firstly, our sensor, as well as devices incorporating PVC membranes (e.g.<sup>15, 23, 24</sup>), display near- Nernstian response only down to a limiting concentration, which sets a limit of detection (LoD) which is approximated as  $c_{st}$  by the Nikolsky-Eisenman equation. As Nikolsky theory relates  $c_{st}$  to the sensitiser rather than the transducer, we propose to dope rrP3HT with ionophores that are known to lead to very low LoD in potentiometric transducers, e.g.<sup>15</sup>. Secondly, the read- out of our sensor is currently not in real time as  $\Delta V_{th}$  is evaluated manually from measured and plotted transfer characteristics. Real- time read- out can be achieved by a constant current source that places the sensitised OTFT in the feedback of an operational amplifier circuit, as for traditional ion- sensitive field effect transistors (ISFETs)<sup>31</sup>.

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