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Electrochemical gating of a hydrophobic organic semiconductor with aqueous media

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Abstract

We show that even the highly hydrophobic semiconducting polymer poly [2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b]thiophene] (PBTTT) can operate in organic electrochemical transistor (OECT) rather than field effect (OFET) mode when gated with aqueous media. The required bulk penetration of anions into the semiconducting film within the electrochemical window of water is here enabled by the choice of anion, namely, picric acid (PA). OECT mode operation in PBTTT films or its analogues had previously been seen only when gated with solid electrolytes with a larger electrochemical window, or for PBTTT analogues with hydrophilic sidechains. We assign the ability of PA anions to penetrate bulk PBTTT from their similarity to PBTTT solvents (chlorinated benzenes), in the sense that they

both display an electron-deficient π electron system. In control experiments, we confirm that OEET mode is not observed when gating PBTTT with another organic acid (acetic acid) that does not display such π electron system, and that the gating mechanism indeed is electrochemical doping rather than a charge transfer mechanism. OEET mode is observed only at rather high PA concentrations in an aqueous gate medium (50 mM or more), but when it is, it leads to conductivities of ≈ 80 S/cm, slightly larger than for a PBTTT analogue with hydrophilic side chains gated with chloride anions.

1-Introduction

Electrolyte-gated (particularly, water-gated) organic thin film transistors (EG/WG OTFTs) have been the subject of intense research recently [e.g. [1-8]. This interest is driven by their potential applications *e.g.* as sensors for waterborne analytes, and in bioelectronics. WG OTFTs can, in principle, operate in two modes, namely an organic field effect transistor (OFET) mode, or an organic electrochemical transistor (OEET) mode[9, 10]. In the OFET mode, a gate voltage applied across the electrolyte leads to interfacial electric double layers (EDLs) at the gate/water interface, and the water/semiconductor interface. The latter consists of an excess of one type of ions in the water, and an opposing charge carrier accumulation layer at the semiconductor surface. In principle, this can be anions *vs.* holes or cations *vs.* electrons, however, practical WG OFETs usually are hole transporting. A negative gate voltage, when exceeding a transistor-specific threshold, will generate hole accumulation and conductivity in the transistor channel: WG OFETs work in accumulation mode.

Transconductance is proportional to the EDL capacitance, C_i , ($\approx 3 \mu\text{F}/\text{cm}^2$ for water gating [1]), but independent of semiconductor film thickness, d . In contrast, in OEET mode, the gate

voltage does not lead to an interfacial EDL, but drives ions across the electrolyte/semiconductor interface into the bulk of the semiconductor. **(Rev 2/2)** OECT mode operation is further divided into ‘depletion mode’ and ‘accumulation mode’. In accumulation mode, ions dope a previously undoped semiconductor channel; in depletion mode, ions de-dope a previously doped channel [8, 11]. As we now have bulk- rather than interfacial transport, transconductance is proportional to dC^* , where C^* is a capacitance per unit volume, and d the thickness of the semiconductor film. A 130 nm film of the synthetic metal PEDOT:PSS displays $dC^* \approx 500 \mu\text{F}/\text{cm}^2$ [12], 2 orders of magnitude larger than C_i in field-effect mode, leading to correspondingly larger ‘on’ currents. This also gives a simple experimental criterion to distinguish OFET from OECT operation, namely that OFET current is smaller and independent of semiconductor film thickness, d , while OECT current is larger, and increases with d .

(Rev 2/2) If a WG TFT operates in OFET- or OECT mode, it is usually controlled by the hydrophobicity or hydrophilicity of the respective organic semiconductor. Among the commonly used thiophene-based organic hole transporters, polymers with thiophene or thiophene-thieno-thiophene conjugated backbones [13] and aliphatic sidechains (e.g. regioregular poly(3-hexithiophene) (rrP3HT) or poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT)) typically lead to field-effect operation [1, 4, 6, 14] due to their hydrophobic nature: the water contact angle with PBTTT and rrP3HT is 107° [15]. However, when the polymer backbone consists of thiophenes carrying more hydrophilic ether crowns (e.g. in PEDOT:PSS [12]), or of a thiophene-thieno-thiophene backbone with hydrophilic side chains, (e.g. in poly(2-(3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[2,2'-bithiophen]-5-yl)thieno [3,2-*b*]thiophene), p(g2T-TT)) [16], OECT mode is observed (depletion mode for PEDOT:PSS, accumulation mode for p(g2T-TT)). However, the distinction between OFET and OECT mode is somewhat fluid and may be crossed. For

example, poly(2-(3,3'-bis(tetradecyloxy)-[2,2'-bithiophen]-5-yl) thieno[3,2-b]thiophene), p(a2T-TT) acts in field-effect mode at low gate voltages and shows OECT mode at high gate voltages [16], and Giridharagopal *et al* report some penetration of chloride ions into bulk even for the hydrophobic rrP3HT [17] under high ion concentrations (~100 mM). However, the highly crystalline and hydrophobic semiconducting polymer PBTTT has so far not been found to operate in OECT mode when gated with aqueous media, not even under (100...200) mM chloride electrolytes [4, 15]. PBTTT OECT operation has been seen previously only when gated with solid electrolyte, PEO: LiClO₃, but with a threshold outside the 1.23 V electrochemical window of water [18].

Here, we report that even PBTTT can work in OECT mode when gated with aqueous media, without the 'sidechain engineering' (hydrophilic *vs* alkane side chains) shown by Giovanetti *et al* [16]. This is achieved by the choice of anion in the gating water, namely the water soluble explosive, picric acid (PA), at high concentrations (\approx 50 mM or more, see below). PA **Rev (3/2)** partially dissociates and dissolves when in contact with water. Otherwise, it is somewhat similar to the few known solvents for PBTTT: PA consists of an electron deficient π electron system due to substitution of a phenol ring with 3 electron withdrawing nitro groups (inset Fig. 1). PBTTT solvents are di- and tri-chlorinated benzene (DCB / TCB). We show that PA's combination of properties - solubility **Rev (3/2)** in water, and similarity to PBTTT solvents - leads to OECT behaviour in PBTTT which has previously shown OFET behaviour only when gated with aqueous media.

2- Experimental details

2.1 Materials: Poly (2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b]thiophene) (PBTTT-C16) was sourced from Ossila Ltd, regioregular poly(3-hexylthiophene) and 0.9 -1.1% (alkalimetric) Picric Acid (2,4,6-Trinitrophenol) solution were sourced from Sigma Aldrich.

2.2 Sample preparation:

Transistor substrates consist of silica-coated glass substrates with shadow-mask evaporated 100 nm Au on 10 nm Cr adhesion layer contact pairs of width $W = 1$ mm separated by a gap ('channel') of $L = 30\mu\text{m}$, $W/L = 33.3$. We have used the same substrates previously for water-gated TFTs [3-5]. PBTTT was dissolved in 1, 2 dichlorobenzene (DCB) at 7 mg/ml or 10 mg/mL respectively, and spin coated onto contact substrates from hot (100 °C) DCB for 40 seconds at 5000 rpm or 2500 rpm for thicker films. After casting, films were dried under dynamic vacuum at 110 °C for 40 minutes. Film thickness was determined with a Veeco Dektak XT surface contact profilometer as 17.6 nm for 5000 rpm and 27 nm for 2500 rpm. For rrP3HT films, we dissolved 10 mg/mL rrP3HT in DCB, heated at 80 °C for ≈ 10 min, and spin cast onto contact substrates at 2000 rpm for 60s. After casting, films were dried under dynamic vacuum at 110 °C for 40 min. Film thickness was 22 nm. The semicrystalline morphology of PBTTT and rrP3HT films have been studied in detail before, *e.g.* [19, 20]. Aqueous Picric Acid solution was sourced at concentration 4.4 M; a 100 mM stock solution was prepared by dilution with DI water. A Eutech Instruments CyberScan pH meter shows $\text{pH} = 5.5$ for 100 mM PA. The 100 mM PA solution was then further diluted in several steps down to 1 μM .

2.3 Electrical characterisation

We applied 2 μL droplets of aqueous test solutions as gate media over the channel region of PBTTT and rrP3HT TFT substrates and electrically addressed by Au gate needles (American Probe and Technologies) bent into an L-shape and held at fixed distance ($\sim 100\mu\text{m}$) from the semiconductor surface using a probehead. Then, we recorded output characteristic and transfer characteristics using two Keithley 2400 source- measure units and bespoke LabView

software. We limited voltage sweeps to 1V rather than the full ‘electrochemical window’ of water of 1.23 V. The setup is shown schematically in Fig. 1.

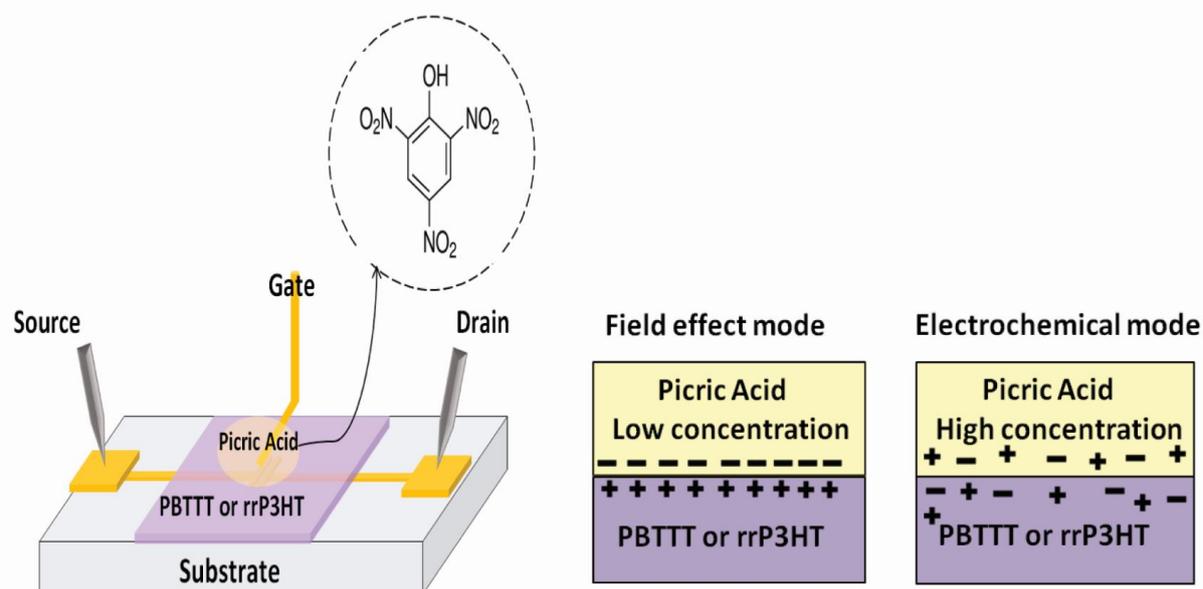


Fig. 1: TFTs gated by aqueous picric acid (PA) solutions. **Inset:** the structure of PA. Field effect (interfacial) and electrochemical (volumetric) transistor mode are illustrated schematically on the right.

(Rev 3/3) - We have deleted the part of (2.4 Optical spectroscopy) from our manuscript.

3 - Results and Discussion

Fig. 2 shows transistor output characteristics for PBTTT and rrP3HT transistors when gated either with DI water, or 100 mM aqueous picric acid solutions. DI water-gated transistors display output characteristics with low threshold and some hysteresis, with maximum currents in the order of a few μA , similar to typical WG OFETs using thiophene-based polymers as semiconductors when we account for different geometry factors W/L (here, $W/L = 33.3$) [1, 21]. As expected, these devices behave as electrolyte-gated field effect transistors. However, when we gate identically prepared films with aqueous solution of 100 mM picric

acid (PA), we now find significantly larger ‘on’ currents in the order mA, and also stronger hysteresis and a dependency on film thickness. The highest observed current is approximately $I_{\text{MAX}} = -7 \text{ mA}$ at $V_G = V_D = -1 \text{ V}$ in Fig. 2b. This corresponds to a sheet resistance of $R_{\square} = 4.7 \text{ k}\Omega/\square$. **(Rev 2/3)** As sheet resistance is related to conductivity σ by $\sigma = 1/(R_{\square}d)$ with film thickness d , here $d = 27 \text{ nm}$, this corresponds to a conductivity of $\sigma \approx 80 \text{ S/cm}$. **(Editor)** This almost reaches the conductivity of commercial PEDOT:PSS synthetic metal products from Heraeus Holding GmbH (Hanau, Germany) for which the technical documentation currently shows conductivity 100 to 1000 S/cm. Such high currents and conductivities can only be understood by volumetric (OECT) gating rather than interfacial (OFET) operation. We note, however, that devices still clearly behave as transistors, not as low resistance resistors, as would be the case for a highly doped semiconductor or synthetic metal: drain current strongly depends on gate voltage. **(Rev 1/1)** The assignment of OFET vs OECT behaviour is supported by comparing results between transistors with two different PBTTT film thicknesses, 27 vs 17.6 nm. The DI water gated transistors show virtually identical maximum current of $\approx 3.5 \mu\text{A}$ for both thicknesses, as expected for OFET mode operation, as field effect is limited to a thin interfacial accumulation layer. However, OECTs display bulk transport, and correspondingly, maximum current is far bigger, and increases with film thickness.

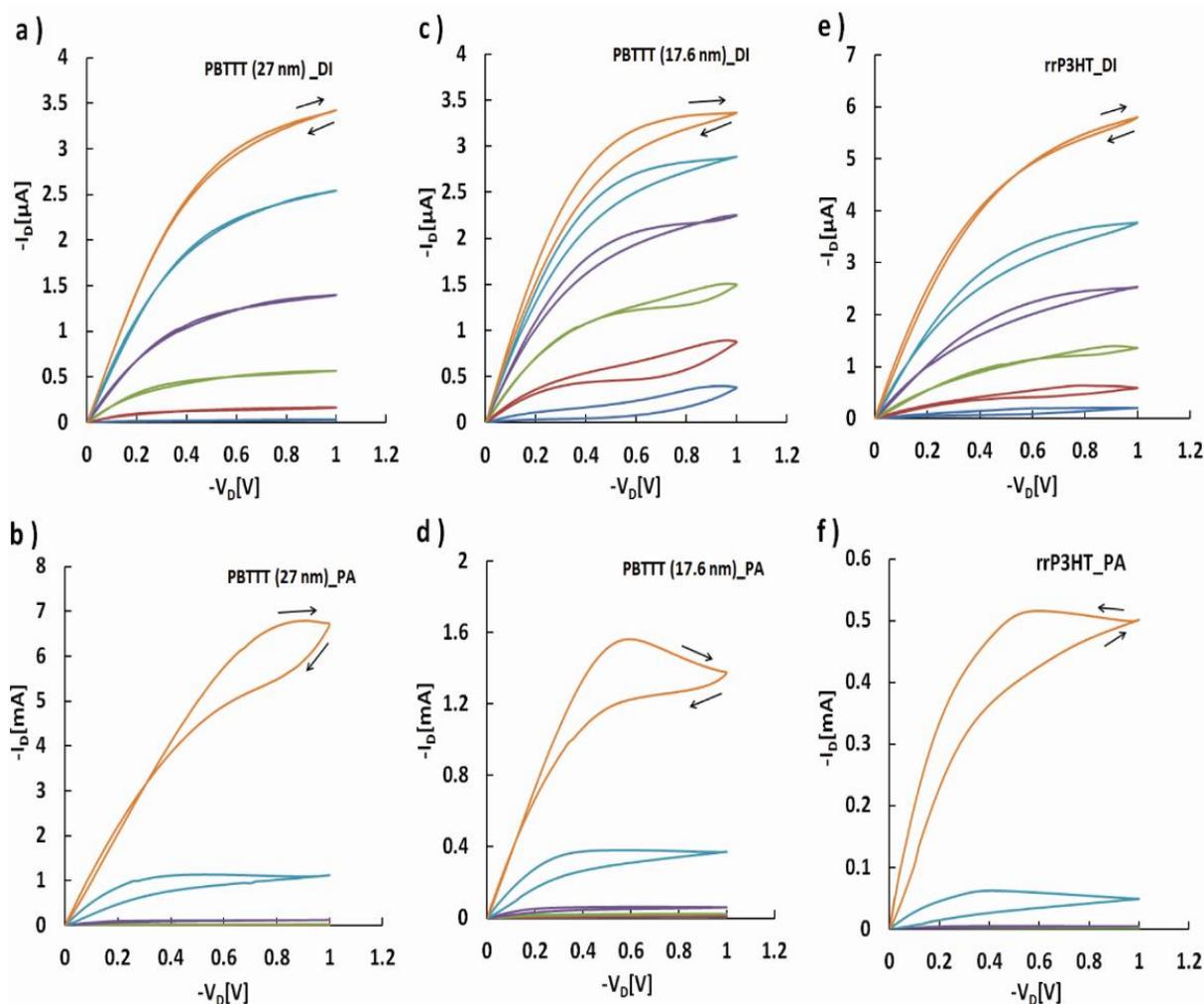


Fig 2: Output characteristic for 27 nm PBT TT film gated by DI water (a) and 100 mM PA (b); 17.6 nm PBT TT film gated by DI water (c) and 100 mM PA (d); and 22nm rrP3HT film gated with DI water (e) and 100 mM PA (f). Note the μA current scale in a,c,e vs mA current scale in b, d, e. Gate voltages from 0 to -1V in steps of 0.2V.

(Rev 3/1) We note that the transition from OFET- to OECT behaviour is specific to gating with PA^- anion, and is not found when PBT TT is gated with a simple anion (e.g. Cl^-), even at high concentration and voltages: Porazzo *et al.* [15] find no evidence of electrochemical gating mode for PBT TT under 200 mM NaCl up to $V_G = -1.2$ V, $V_D = -1$ V, Fig. 3 in [15].

To confirm, we have repeated the above experiments three times on nominally identical devices. The resulting I_{MAX} are shown on a logarithmic scale in Fig. 3.

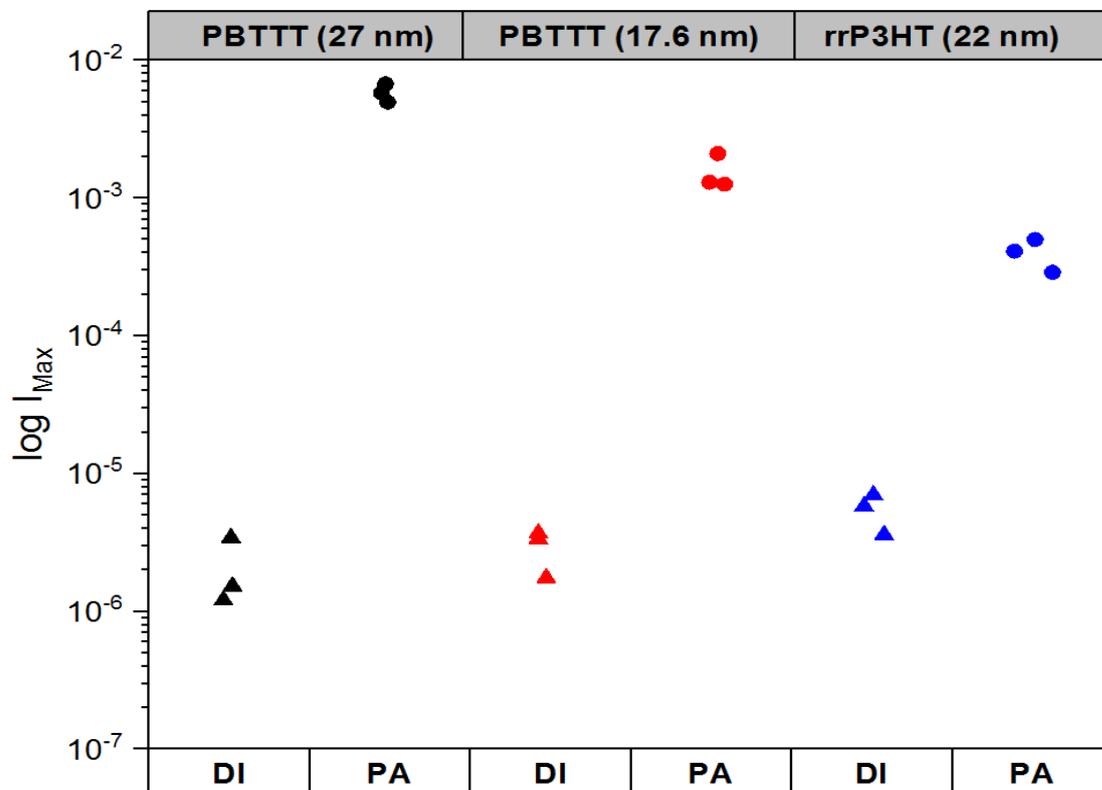


Fig 3: Saturated drain current at $V_G = -1V$ (I_{MAX}) from output characteristics of 3 nominally identical transistors each, comparing films of PBT TT (27 nm, black), PBT TT (17.6 nm, red) and rrP3HT (22 nm, blue) gated with either DI water (triangles) or 100 mM picric acid (PA, circles) solution in water. Note the logarithmic current scale.

We find that in all cases, 100mM PA gating leads to significantly higher drain current than DI water gating, more so for PBT TT than for rrP3HT. Also, thicker PBT TT films give higher currents than thinner PBT TT films. All these observations suggest that when gated with 100 mM PA, PBT TT and rrP3HT based thin film transistors operate in electrochemical (OECT)

rather than field effect mode. Unlike e.g. chloride ions [4, 15], PA anions apparently are able to penetrate the bulk of PBTTT films despite PBTTT's strongly hydrophobic character.

We find, however, that this is only the case at sufficiently high concentrations of PA. Fig. 4 shows saturated transistor drain currents (at $V_G = -0.8$ V) against PA concentration in water.

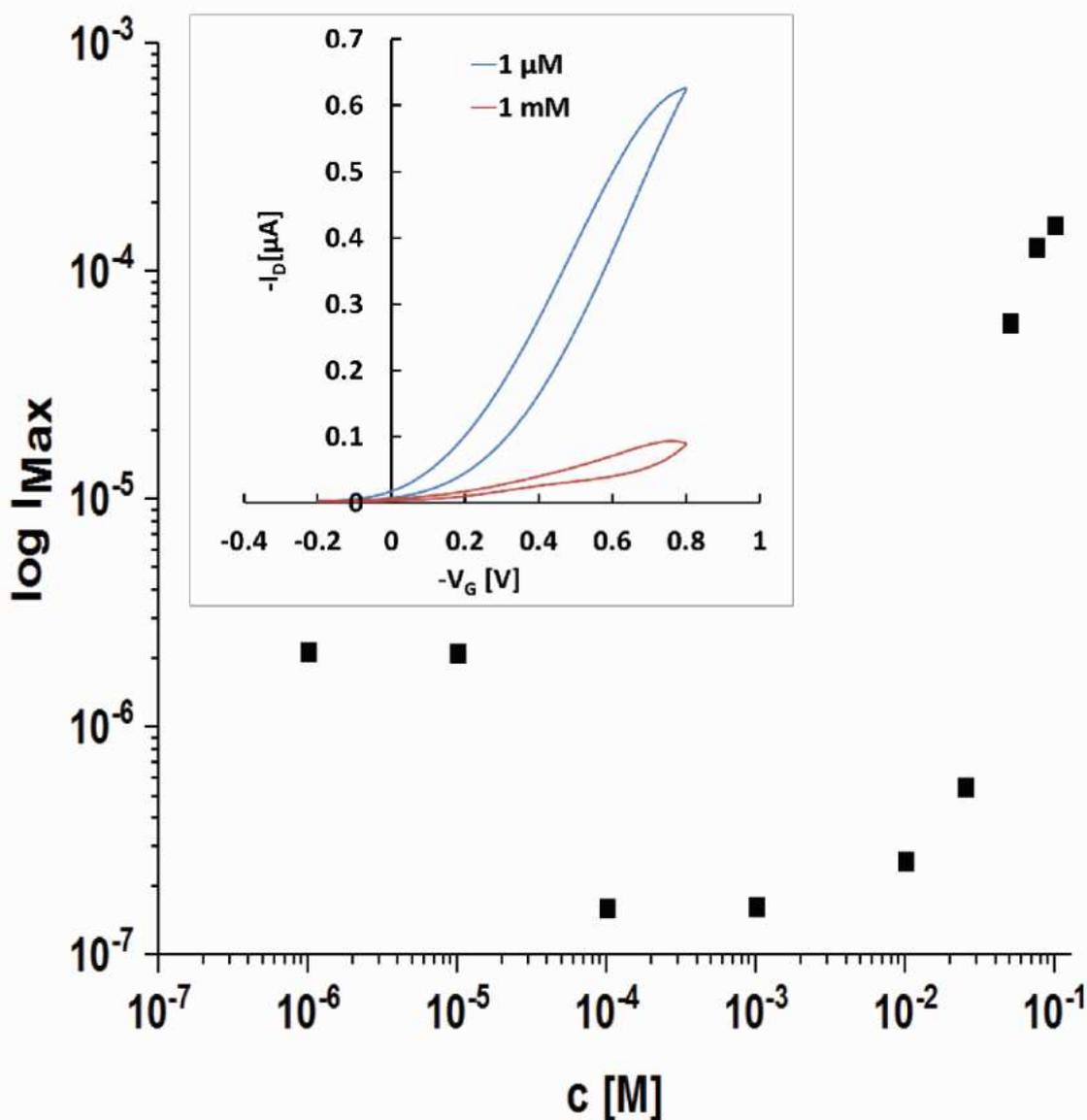


Fig. 4: Saturated drain current (I_{MAX}) at $V_G = -0.8$ V on logarithmic scale vs. PA concentration in gating water, also on logarithmic scale. Inset: Linear transfer characteristics ($V_D = -0.1$ V) for 1 μM (blue) and 1 mM (red) PA concentration.

For PA concentrations c from zero up to 1mM, saturated drain current remains low, and in fact somewhat decreases with increasing c . (**Rev 1/2**) At low PA concentrations, the transistor still operates in field effect mode, *i.e.* gating is via an interfacial EDL, therefore, the transition to electrochemical mode seen in Fig. 2 requires higher PA concentrations. The linear transfer characteristics shown in the inset show lower mobility (slope) and larger threshold (V_G axis intercept) under 1 mM vs. 1 μ M PA. This is probably due to interactions between the electron-deficient π electron system of PA with PBTTT at the semiconductor/water EDL; such an effect is absent when the EDL forms with a ‘simple’ anion like chloride [4]. However, there is a rather sharp transition to far higher drain currents beginning at 10 mM PA concentrations, which is completed at $c \approx 50$ mM. We assign this to the transition from field effect to electrochemical transistor mode under high PA concentrations. (**Rev 2/ 1**) EDL gating requires only a single sheet of ions at the gate medium /semiconductor interface, hence EDLs can build up even from gate media with minute ion concentrations [22]. In contrast, electrochemical gating requires bulk doping of the solid semiconducting film, hence far larger numbers of ions have to be supplied from the gate medium. Electrochemical gate media reported in the literature often have ion concentrations in the order 100 mM [11, 16]. In the case of PBTTT doped with PA, it seems $c \approx 50$ mM of PA in the gate medium is needed to supply sufficient anions for electrochemical doping. (**Rev 3/2**) We note, however, that the PA concentrations we report here are concentrations of PA molecules dissolved in water, not of dissociated anions, PA^- . Unlike simple salts, organic acids dissociate only partly in water, $PA + H_2O \rightleftharpoons PA^- + H_3O^+$. This is evident from pH measurements, we find $pH \approx 5.5$ for 100 mM PA, full dissociation would lead to $pH = -\log(0.1) = 1$; note $pH = p(\text{anion})$. The dissociation equilibrium is weighted towards the molecule (PA) rather than the anion (PA^-) by about 30,000: 1. The minimum concentration of PA^-

anions required to affect electrochemical gating is therefore significantly lower than the quoted $c \approx 50$ mM concentration of PA *molecules*.

As a control experiment, we have gated a PBTTT film with another organic acid, acetic acid, at significantly higher concentration (**Rev 3/2**), of 5% acetic acid ≈ 870 mM. Again, acetic acid dissociates only partially; $-\log(0.87) \approx 0.1$ but we measure $\text{pH} = 2.6$. Nevertheless, the concentration of acetic acid anions in the control experiment ($\text{pH} 2.6$) is far higher than concentration of PA^- anions in 100 mM PA solution ($\text{pH} 5.5$). Fig. 5 shows output characteristics under 5% acetic acid gating:

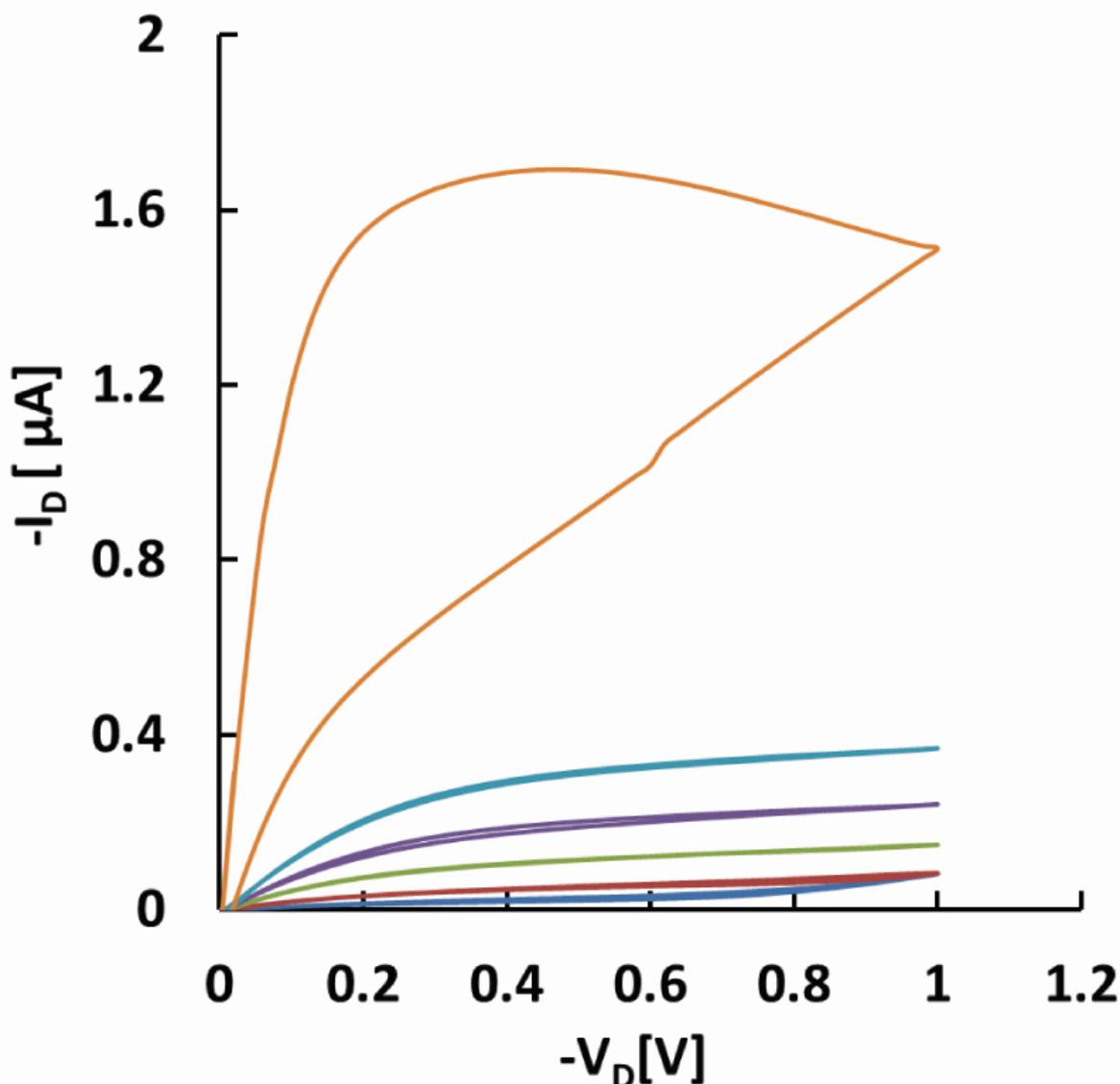


Fig 5: Output characteristic of PBTTT under 5% acetic acid (commercial vinegar condiment, pH = 2.6)

We find large hysteresis at high gate voltage but currents remain in the μA range. The acetic acid anion does not lead to OECT operation, just like the chloride anion did not in previous reports [4, 15]. The bulk penetration into PBTTT that leads to OECT mode is specific to the PA^- anion, and is not observed even for other organic acid anions. We believe that this is due to the similarity of the PA^- anion to PBTTT solvents (chlorinated benzenes), apart from the ionic vs. neutral character: They both display an electron-deficient π electron system. This similarity is not shared by chloride (**Rev 1/4**) or acetic acid anions. The acetic acid control experiment shows that the ‘organic acid anion’ property alone is not sufficient to enable bulk penetration of PBTTT.

(**Rev 3/3**) On careful consideration, we find that Fig. 6 does not contribute to our conclusions. As we extended the manuscript in response to other points, we therefore decided to delete Fig. 6.

4- Conclusion

We show that even the highly hydrophobic semiconducting polymer poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT) can operate in organic electrochemical transistor (OECT) rather than field effect (OFET) mode when gated with aqueous media. The required bulk penetration of anions into the semiconducting film within the electrochemical window of water is enabled here by the choice of anion, namely, picric acid (PA). OECT mode operation in PBTTT films or its analogues had previously been seen only when gated with solid electrolytes with a larger electrochemical window [18], or for PBTTT analogues with hydrophilic sidechains [16]. (**Rev 2/4**) There, hydrophilicity allows some penetration of water into semiconductor bulk, which then carries with it ions that lead

to bulk gating. Here, we find bulk gating despite the inability of water to penetrate the highly hydrophobic PBTTT. We believe that PA⁻ anions can penetrate PBTTT bulk without using water as a 'vector'. We assign this ability to the similarity of PA to solvents for PBTTT, namely chlorinated benzenes: both PA, and chlorinated benzenes, display an electron-deficient π electron system. In control experiments, we confirm that OECT mode is not observed when gating PBTTT with a different organic acid (acetic acid) that does not display such π electron system, and that the gating mechanism indeed is electrochemical doping rather than a charge transfer mechanism. OECT mode is observed only at rather high PA concentrations in the gate medium (50 mM or more), (**Rev 3/2**) albeit the weak dissociation of PA into anions means this corresponds to a rather lower concentration of PA⁻ anions. When OECT mode is observed, it leads to conductivities of ≈ 80 S/cm, slightly larger than for p(g2T-TT), a PBTTT analogue with hydrophilic side chains gated with chloride anions [16].

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ACCEPTED MANUSCRIPT

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Abstract

We show that even the highly hydrophobic semiconducting polymer poly [2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b]thiophene] (PBTTT) can operate in organic electrochemical transistor (OECT) rather than field effect (OFET) mode when gated with aqueous media. The required bulk penetration of anions into the semiconducting film within the electrochemical window of water is here enabled by the choice of anion, namely, picric

acid (PA). OECT mode operation in PBTTT films or its analogues had previously been seen only when gated with solid electrolytes with a larger electrochemical window, or for PBTTT analogues with hydrophilic sidechains. We assign the ability of PA anions to penetrate bulk PBTTT from their similarity to PBTTT solvents (chlorinated benzenes), in the sense that they both display an electron-deficient π electron system. In control experiments, we confirm that OECT mode is not observed when gating PBTTT with another organic acid (acetic acid) that does not display such π electron system, and that the gating mechanism indeed is electrochemical doping rather than a charge transfer mechanism. OECT mode is observed only at rather high PA concentrations in an aqueous gate medium (50 mM or more), but when it is, it leads to conductivities of ≈ 80 S/cm, slightly larger than for a PBTTT analogue with hydrophilic side chains gated with chloride anions.

1-Introduction

Electrolyte-gated (particularly, water-gated) organic thin film transistors (EG/WG OTFTs) have been the subject of intense research recently [e.g. [1-8]. This interest is driven by their potential applications *e.g.* as sensors for waterborne analytes, and in bioelectronics. WG OTFTs can, in principle, operate in two modes, namely an organic field effect transistor (OFET) mode, or an organic electrochemical transistor (OECT) mode[9, 10]. In the OFET mode, a gate voltage applied across the electrolyte leads to interfacial electric double layers (EDLs) at the gate/water interface, and the water/semiconductor interface. The latter consists of an excess of one type of ions in the water, and an opposing charge carrier accumulation layer at the semiconductor surface. In principle, this can be anions *vs.* holes or cations *vs.* electrons, however, practical WG OFETs usually are hole transporting. A negative gate voltage, when exceeding a transistor-specific threshold, will generate hole accumulation and

conductivity in the transistor channel: WG OFETs work in accumulation mode.

Transconductance is proportional to the EDL capacitance, C_i , ($\approx 3 \mu\text{F}/\text{cm}^2$ for water gating [1]), but independent of semiconductor film thickness, d . In contrast, in OECT mode, the gate voltage does not lead to an interfacial EDL, but drives ions across the electrolyte/semiconductor interface into the bulk of the semiconductor. OECT mode operation is further divided into ‘depletion mode’ and ‘accumulation mode’. In accumulation mode, ions dope a previously undoped semiconductor channel; in depletion mode, ions dedope a previously doped channel [8, 11]. As we now have bulk- rather than interfacial transport, transconductance is proportional to dC^* , where C^* is a capacitance per unit volume, and d the thickness of the semiconductor film. A 130 nm film of the synthetic metal PEDOT:PSS displays $dC^* \approx 500 \mu\text{F}/\text{cm}^2$ [12], 2 orders of magnitude larger than C_i in field-effect mode, leading to correspondingly larger ‘on’ currents. This also gives a simple experimental criterion to distinguish OFET from OECT operation, namely that OFET current is smaller and independent of semiconductor film thickness, d , while OECT current is larger, and increases with d .

If a WG TFT operates in OFET- or OECT mode, it is usually controlled by the hydrophobicity or hydrophilicity of the respective organic semiconductor. Among the commonly used thiophene-based organic hole transporters, polymers with thiophene or thiophene-thieno-thiophene conjugated backbones[13] and aliphatic sidechains (e.g. regioregular poly(3-hexithiophene) (rrP3HT) or poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT)) typically lead to field-effect operation [1, 4, 6, 14] due to their hydrophobic nature: the water contact angle with PBTTT and rrP3HT is 107° [15]. However, when the polymer backbone consists of thiophenes carrying more hydrophilic ether crowns (e.g. in PEDOT:PSS [12]), or of a thiophene-thieno-thiophene backbone with hydrophilic side chains, (e.g. in poly(2-(3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-

[2,2'-bithiophen]-5-yl) thieno [3,2-b]thiophene), p(g2T-TT)) [16], OECT mode is observed (depletion mode for PEDOT:PSS, accumulation mode for p(g2T-TT)). However, the distinction between OFET and OECT mode is somewhat fluid and may be crossed. For example, poly(2-(3,3'-bis(tetradecyloxy)-[2,2'-bithiophen]-5-yl) thieno[3,2-b]thiophene), p(a2T-TT) acts in field-effect mode at low gate voltages and shows OECT mode at high gate voltages [16], and Giridharagopal *et al* report some penetration of chloride ions into bulk even for the hydrophobic rrP3HT [17] under high ion concentrations (~100 mM). However, the highly crystalline and hydrophobic semiconducting polymer PBTTT has so far not been found to operate in OECT mode when gated with aqueous media, not even under (100...200) mM chloride electrolytes [4, 15]. PBTTT OECT operation has been seen previously only when gated with solid electrolyte, PEO: LiClO₃, but with a threshold outside the 1.23 V electrochemical window of water [18].

Here, we report that even PBTTT can work in OECT mode when gated with aqueous media, without the 'sidechain engineering' (hydrophilic vs alkane side chains) shown by Giovanetti *et al* [16]. This is achieved by the choice of anion in the gating water, namely the water soluble explosive, picric acid (PA), at high concentrations (\approx 50 mM or more, see below). PA partially dissociates and dissolves when in contact with water. Otherwise, it is somewhat similar to the few known solvents for PBTTT: PA consists of an electron deficient π electron system due to substitution of a phenol ring with 3 electron withdrawing nitro groups (inset Fig. 1). PBTTT solvents are di- and tri-chlorinated benzene (DCB / TCB). We show that PA's combination of properties - solubility in water, and similarity to PBTTT solvents - leads to OECT behaviour in PBTTT which has previously shown OFET behaviour only when gated with aqueous media.

2- Experimental details

2.1 Materials: Poly (2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b]thiophene) (PBTTT-C16) was sourced from Ossila Ltd, regioregular poly(3-hexylthiophene) and 0.9 -1.1% (alkalimetric) Picric Acid (2,4,6-Trinitrophenol) solution were sourced from Sigma Aldrich.

2.2 Sample preparation:

Transistor substrates consist of silica-coated glass substrates with shadow-mask evaporated 100 nm Au on 10 nm Cr adhesion layer contact pairs of width $W = 1$ mm separated by a gap ('channel') of $L = 30\mu\text{m}$, $W/L = 33.3$. We have used the same substrates previously for water-gated TFTs [3-5]. PBTTT was dissolved in 1, 2 dichlorobenzene (DCB) at 7 mg/ml or 10 mg/mL respectively, and spin coated onto contact substrates from hot (100 °C) DCB for 40 seconds at 5000 rpm or 2500 rpm for thicker films. After casting, films were dried under dynamic vacuum at 110 °C for 40 minutes. Film thickness was determined with a Veeco Dektak XT surface contact profilometer as 17.6 nm for 5000 rpm and 27 nm for 2500 rpm. For rrP3HT films, we dissolved 10 mg/mL rrP3HT in DCB, heated at 80 °C for ≈ 10 min, and spin cast onto contact substrates at 2000 rpm for 60s. After casting, films were dried under dynamic vacuum at 110 °C for 40 min. Film thickness was 22 nm. The semicrystalline morphology of PBTTT and rrP3HT films have been studied in detail before, *e.g.* [19, 20]. Aqueous Picric Acid solution was sourced at concentration 4.4 M; a 100 mM stock solution was prepared by dilution with DI water. A Eutech Instruments CyberScan pH meter shows $\text{pH} = 5.5$ for 100 mM PA. The 100 mM PA solution was then further diluted in several steps down to $1\mu\text{M}$.

2.3 Electrical characterisation

We applied 2 μL droplets of aqueous test solutions as gate media over the channel region of PBTTT and rrP3HT TFT substrates and electrically addressed by Au gate needles (American Probe and Technologies) bent into an L-shape and held at fixed distance ($\sim 100\mu\text{m}$) from the semiconductor surface using a probehead. Then, we recorded output characteristic and transfer characteristics using two Keithley 2400 source-measure units and bespoke LabView software. We limited voltage sweeps to 1V rather than the full ‘electrochemical window’ of water of 1.23 V. The setup is shown schematically in Fig. 1.

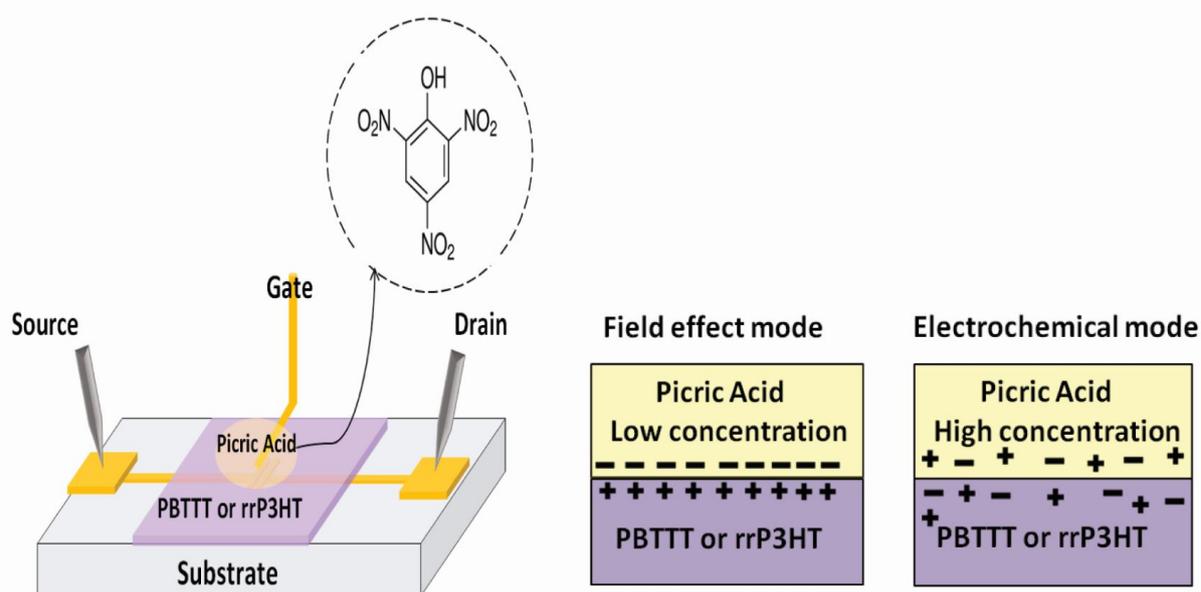


Fig. 1: TFTs gated by aqueous picric acid (PA) solutions. **Inset:** the structure of PA. Field effect (interfacial) and electrochemical (volumetric) transistor mode are illustrated schematically on the right.

3 - Results and Discussion

Fig. 2 shows transistor output characteristics for PBTTT and rrP3HT transistors when gated either with DI water, or 100 mM aqueous picric acid solutions. DI water-gated transistors display output characteristics with low threshold and some hysteresis, with maximum currents in the order of a few μA , similar to typical WG OFETs using thiophene-based

polymers as semiconductors when we account for different geometry factors W/L (here, $W/L = 33.3$) [1, 21]. As expected, these devices behave as electrolyte-gated field effect transistors. However, when we gate identically prepared films with aqueous solution of 100 mM picric acid (PA), we now find significantly larger ‘on’ currents in the order mA, and also stronger hysteresis and a dependency on film thickness. The highest observed current is approximately $I_{MAX} = -7$ mA at $V_G = V_D = -1$ V in Fig. 2b. This corresponds to a sheet resistance of $R_{\square} = 4.7$ k Ω/\square . As sheet resistance is related to conductivity σ by $\sigma = 1/(R_{\square}d)$ with film thickness d , here $d = 27$ nm, this corresponds to a conductivity of $\sigma \approx 80$ S/cm. This almost reaches the conductivity of commercial PEDOT: PSS synthetic metal products from Heraeus Holding GmbH (Hanau, Germany) for which the technical documentation currently shows conductivity 100 to 1000 S/cm. Such high currents and conductivities can only be understood by volumetric (OEET) gating rather than interfacial (OFET) operation. We note, however, that devices still clearly behave as transistors, not as low resistance resistors, as would be the case for a highly doped semiconductor or synthetic metal: drain current strongly depends on gate voltage. The assignment of OFET vs OEET behaviour is supported by comparing results between transistors with two different PBTTT film thicknesses, 27 vs 17.6 nm. The DI water gated transistors show virtually identical maximum current of ≈ 3.5 μ A for both thicknesses, as expected for OFET mode operation, as field effect is limited to a thin interfacial accumulation layer. However, OEETs display bulk transport, and correspondingly, maximum current is far bigger, and increases with film thickness.

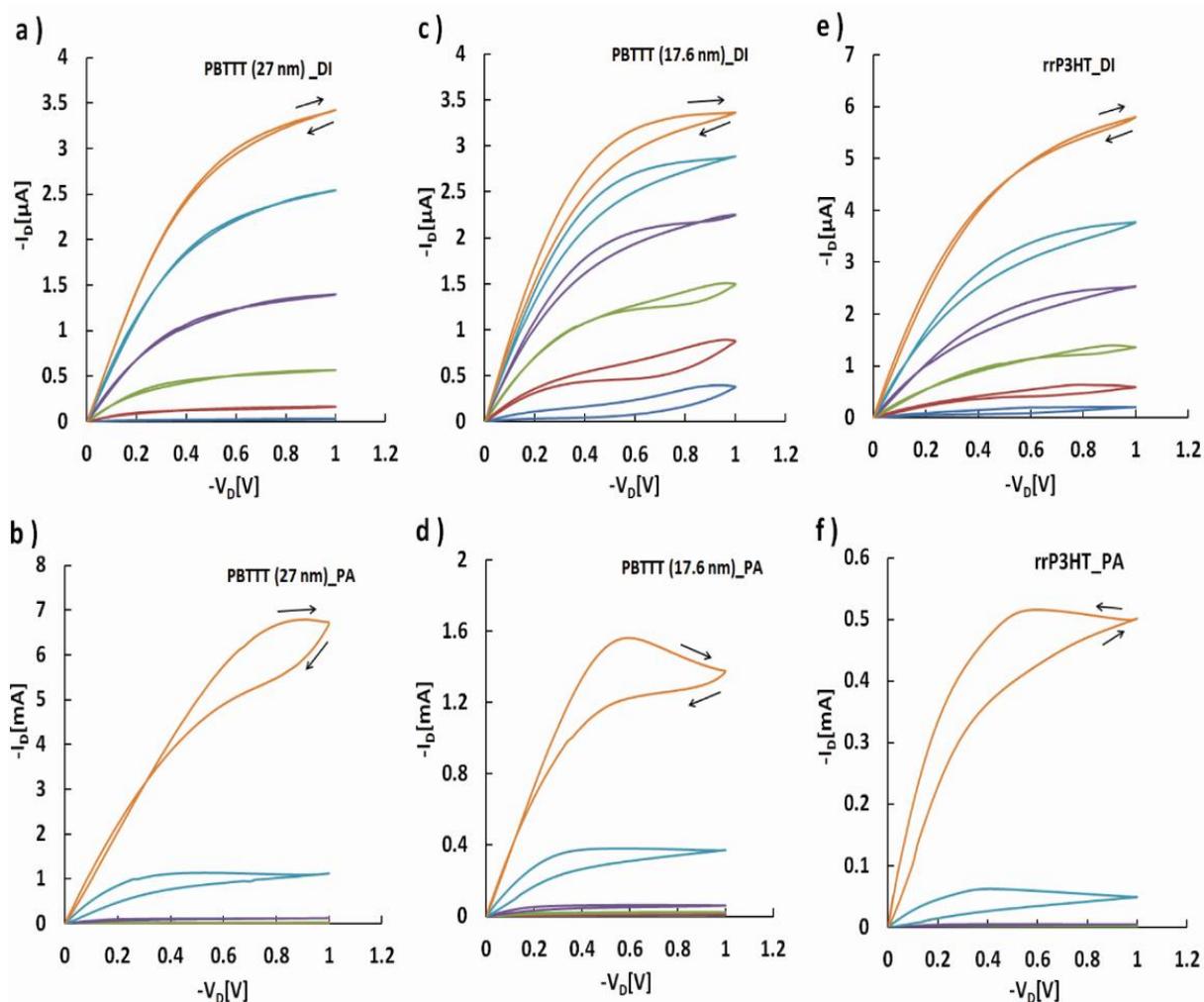


Fig 2: Output characteristic for 27 nm PBTtT film gated by DI water (a) and 100 mM PA (b); 17.6 nm PBTtT film gated by DI water (c) and 100 mM PA (d); and 22nm rrP3HT film gated with DI water (e) and 100 mM PA (f). Note the μA current scale in a,c,e vs mA current scale in b, d, e. Gate voltages from 0 to -1V in steps of 0.2V.

We note that the transition from OFET- to OEET behaviour is specific to gating with PA^- anion, and is not found when PBTtT is gated with a simple anion (e.g. Cl^-), even at high concentration and voltages: Porazzo *et al.* [15] find no evidence of electrochemical gating mode for PBTtT under 200 mM NaCl up to $V_G = -1.2$ V, $V_D = -1$ V, Fig. 3 in [15].

To confirm, we have repeated the above experiments three times on nominally identical devices. The resulting I_{MAX} are shown on a logarithmic scale in Fig. 3.

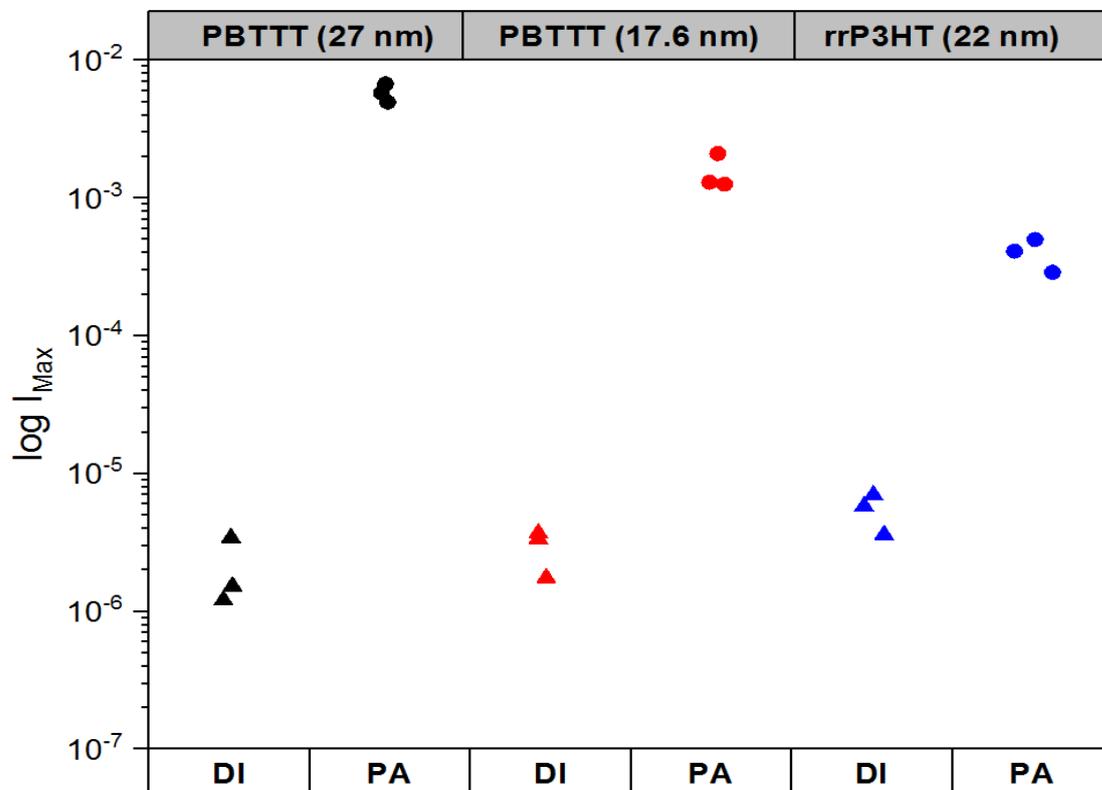


Fig 3: Saturated drain current at $V_G = -1V$ (I_{MAX}) from output characteristics of 3 nominally identical transistors each, comparing films of PBT TT (27 nm, black), PBT TT (18 nm, red) and rrP3HT (22 nm, blue) gated with either DI water (triangles) or 100 mM picric acid (PA, circles) solution in water. Note the logarithmic current scale.

We find that in all cases, 100mM PA gating leads to significantly higher drain current than DI water gating, more so for PBT TT than for rrP3HT. Also, thicker PBT TT films give higher currents than thinner PBT TT films. All these observations suggest that when gated with 100 mM PA, PBT TT and rrP3HT based thin film transistors operate in electrochemical (OECT) rather than field effect mode. Unlike e.g. chloride ions [4, 15], PA anions apparently are able

to penetrate the bulk of PBTTT films despite PBTTT's strongly hydrophobic character.

We find, however, that this is only the case at sufficiently high concentrations of PA. Fig. 4 shows saturated transistor drain currents (at $V_G = -0.8$ V) against PA concentration in water.

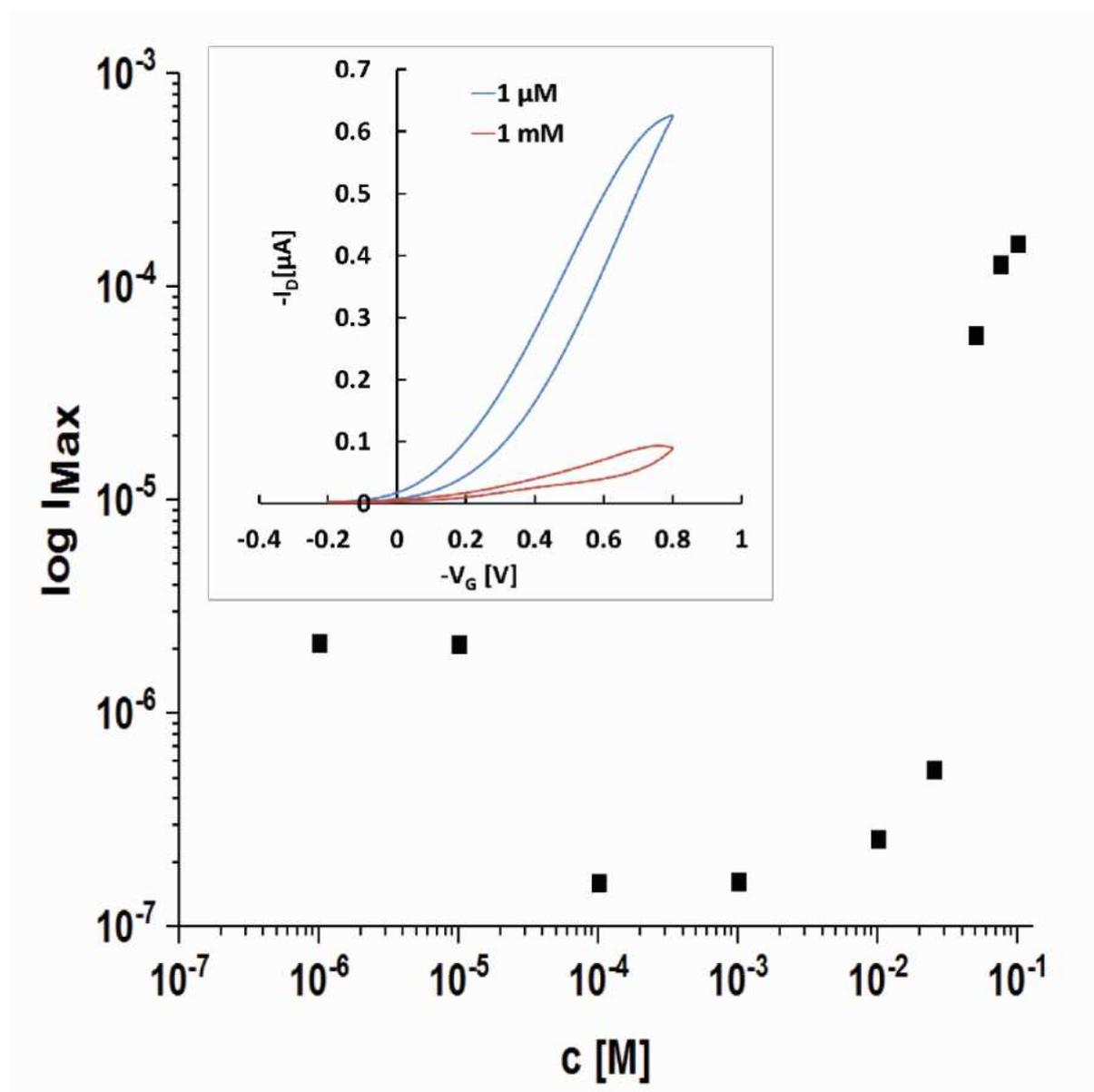


Fig. 4: Saturated drain current (I_{MAX}) at $V_G = -0.8$ V on logarithmic scale vs. PA concentration in gating water, also on logarithmic scale. **Inset:** Linear transfer characteristics ($V_D = -0.1$ V) for $1 \mu M$ (blue) and $1 mM$ (red) PA concentration.

For PA concentrations c from zero up to 1mM, saturated drain current remains low, and in fact somewhat decreases with increasing c . At low PA concentrations, the transistor still operates in field effect mode, *i.e.* gating is via an interfacial EDL, therefore, the transition to electrochemical mode seen in Fig. 2 requires higher PA concentrations. The linear transfer characteristics shown in the inset show lower mobility (slope) and larger threshold (V_G axis intercept) under 1 mM vs. 1 μ M PA. This is probably due to interactions between the electron-deficient π electron system of PA with PBTTT at the semiconductor/water EDL; such an effect is absent when the EDL forms with a ‘simple’ anion like chloride [4]. However, there is a rather sharp transition to far higher drain currents beginning at 10 mM PA concentrations, which is completed at $c \approx 50$ mM. We assign this to the transition from field effect to electrochemical transistor mode under high PA concentrations. EDL gating requires only a single sheet of ions at the gate medium /semiconductor interface, hence EDLs can build up even from gate media with minute ion concentrations [22]. In contrast, electrochemical gating requires bulk doping of the solid semiconducting film, hence far larger numbers of ions have to be supplied from the gate medium. Electrochemical gate media reported in the literature often have ion concentrations in the order 100 mM [11, 16]. In the case of PBTTT doped with PA, it seems $c \approx 50$ mM of PA in the gate medium is needed to supply sufficient anions for electrochemical doping. We note, however, that the PA concentrations we report here are concentrations of PA molecules dissolved in water, not of dissociated anions, PA^- . Unlike simple salts, organic acids dissociate only partly in water, $PA + H_2O \rightleftharpoons PA^- + H_3O^+$. This is evident from pH measurements, we find $pH \approx 5.5$ for 100 mM PA, full dissociation would lead to $pH = -\log(0.1) = 1$; note $pH = p(\text{anion})$. The dissociation equilibrium is weighted towards the molecule (PA) rather than the anion (PA^-) by about 30,000: 1. The minimum concentration of PA^- anions required to affect electrochemical

gating is therefore significantly lower than the quoted $c \approx 50$ mM concentration of PA molecules.

As a control experiment, we have gated a PBTTT film with another organic acid, acetic acid, at significantly higher concentration of 5% acetic acid ≈ 870 mM. Again, acetic acid dissociates only partially; $-\log(0.87) \approx 0.1$ but we measure $\text{pH} = 2.6$. Nevertheless, the concentration of acetic acid anions in the control experiment ($\text{pH} 2.6$) is far higher than concentration of PA^- anions in 100 mM PA solution ($\text{pH} 5.5$). Fig. 5 shows output characteristics under 5% acetic acid gating:

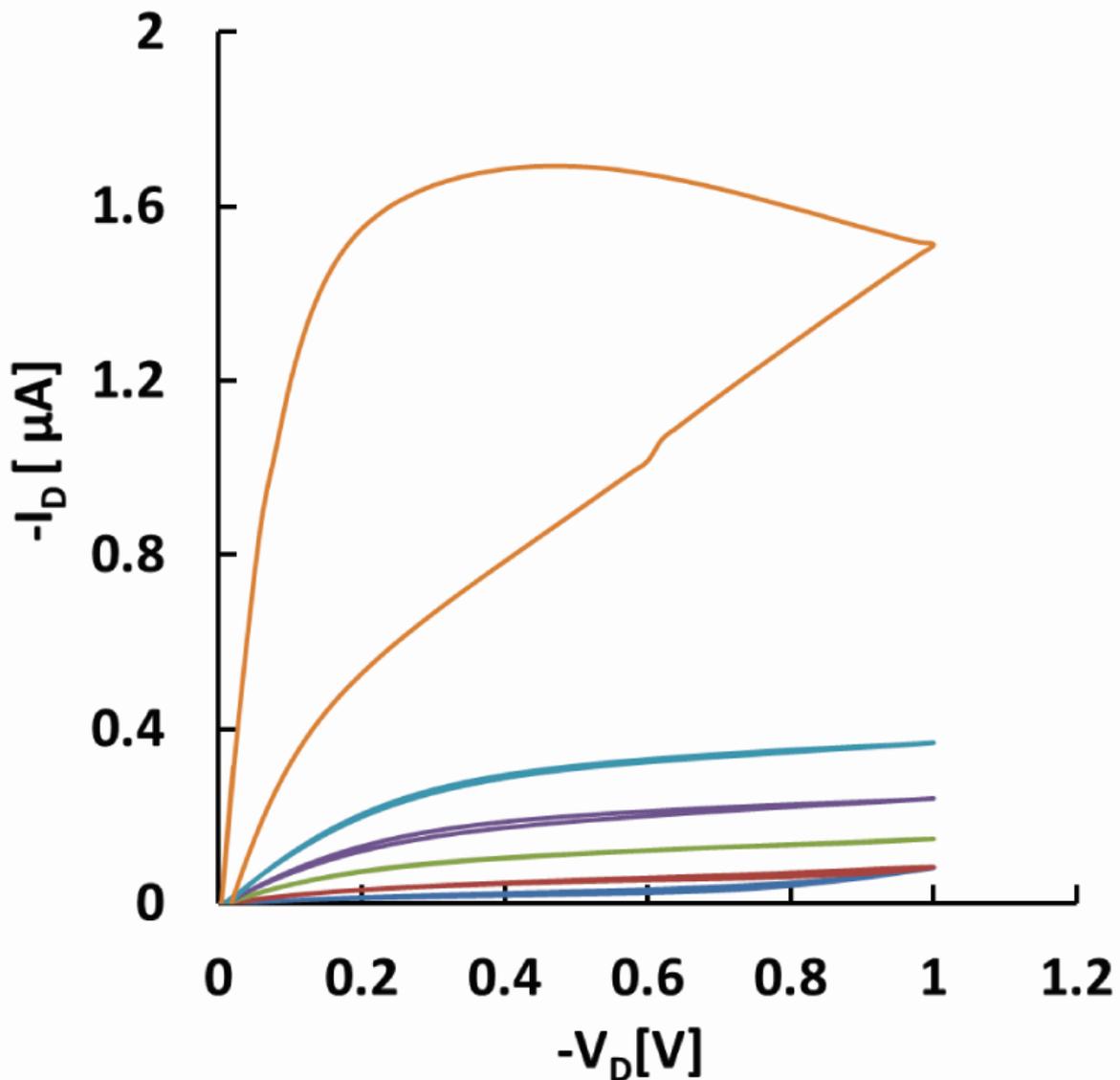


Fig 5: Output characteristic of PBTTT under 5% acetic acid (commercial vinegar condiment, pH = 2.6)

We find large hysteresis at high gate voltage but currents remain in the μA range. The acetic acid anion does not lead to OECT operation, just like the chloride anion did not in previous reports [4, 15]. The bulk penetration into PBTTT that leads to OECT mode is specific to the PA^- anion, and is not observed even for other organic acid anions. We believe that this is due to the similarity of the PA^- anion to PBTTT solvents (chlorinated benzenes), apart from the ionic vs. neutral character: They both display an electron-deficient π electron system. This similarity is not shared by chloride or acetic acid anions. The acetic acid control experiment shows that the ‘organic acid anion’ property alone is not sufficient to enable bulk penetration of PBTTT.

4- Conclusion

We show that even the highly hydrophobic semiconducting polymer poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT) can operate in organic electrochemical transistor (OECT) rather than field effect (OFET) mode when gated with aqueous media. The required bulk penetration of anions into the semiconducting film within the electrochemical window of water is enabled here by the choice of anion, namely, picric acid (PA). OECT mode operation in PBTTT films or its analogues had previously been seen only when gated with solid electrolytes with a larger electrochemical window [18], or for PBTTT analogues with hydrophilic sidechains [16]. There, hydrophilicity allows some penetration of water into semiconductor bulk, which then carries with it ions that lead to bulk

gating. Here, we find bulk gating despite the inability of water to penetrate the highly hydrophobic PBTTT. We believe that PA⁻ anions can penetrate PBTTT bulk without using water as a 'vector'. We assign this ability to the similarity of PA to solvents for PBTTT, namely chlorinated benzenes: both PA, and chlorinated benzenes, display an electron-deficient π electron system. In control experiments, we confirm that OECT mode is not observed when gating PBTTT with a different organic acid (acetic acid) that does not display such π electron system, and that the gating mechanism indeed is electrochemical doping rather than a charge transfer mechanism. OECT mode is observed only at rather high PA concentrations in the gate medium (50 mM or more), albeit the weak dissociation of PA into anions means this corresponds to a rather lower concentration of PA⁻ anions. When OECT mode is observed, it leads to conductivities of ≈ 80 S/cm, slightly larger than for p(g2T-TT), a PBTTT analogue with hydrophilic side chains gated with chloride anions [16].

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ACCEPTED MANUSCRIPT

Highlights

- Hydrophobic semiconducting polymer PBTTT operates in OECT mode when gated with aqueous media.
- Picric acid (PA) anions penetrate bulk PBTTT due to their similarity to PBTTT solvents.
- OECT mode operation requires high PA concentration in aqueous gate medium (50 mM or more).
- When OECT mode is achieved ~ 80 S/cm, conductivity is reached similar to synthetic metals.