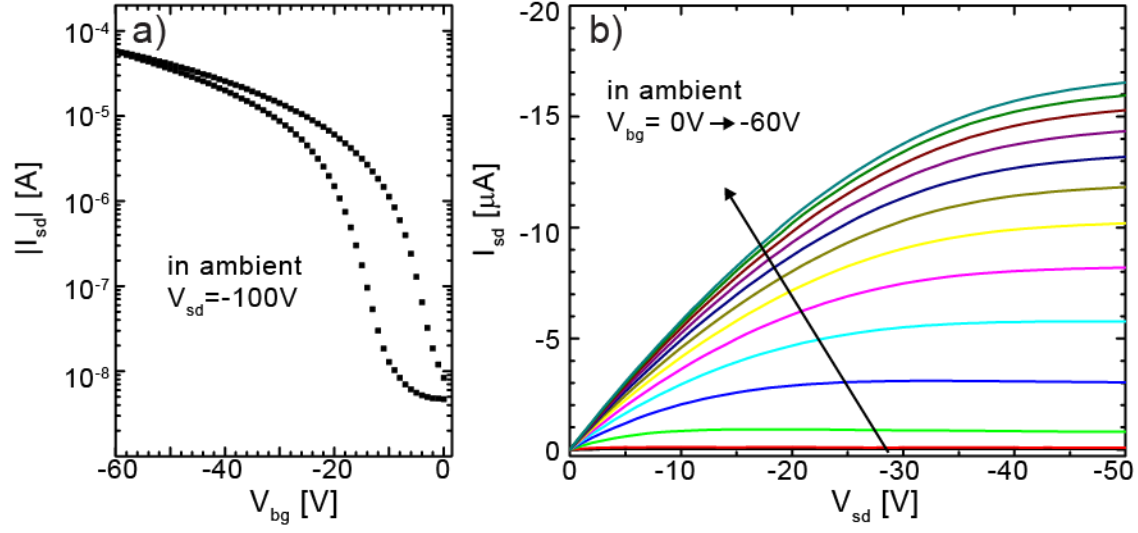
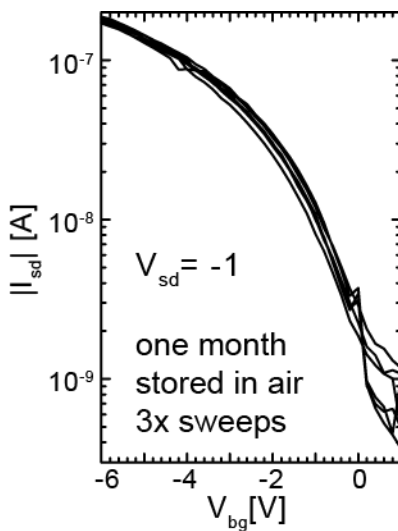
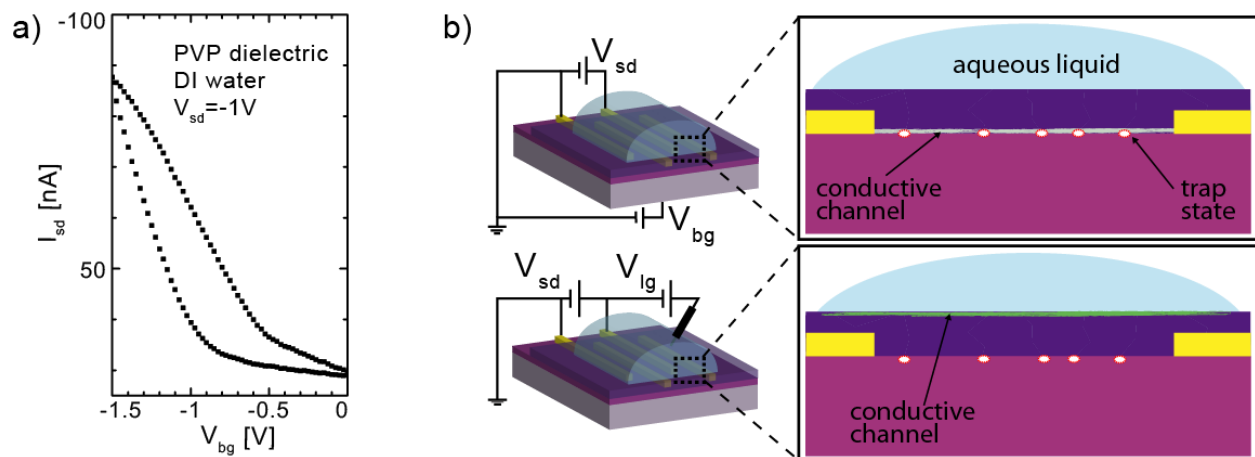




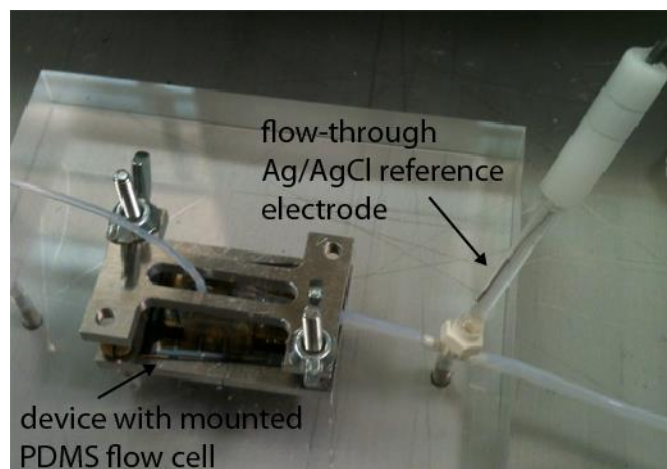
Supplementary Figure S1: Typical electrical performance for high back-gate and source-drain voltages. In **a)** the transfer characteristics I_{sd} vs. applied V_{bg} for constant $V_{sd} = -100$ V is shown while in **b)** the output characteristics I_{sd} vs. V_{sd} for different V_{bg} are shown. We observe similar performance to our previous reported data.³³ Typical mobilities of the fabricated devices at high voltages are in the range of ~ 0.04 cm²/Vs. The lower values of the saturation current and the mobility can be related to the bottom-contact structure and a different device fabrication process used in this manuscript.



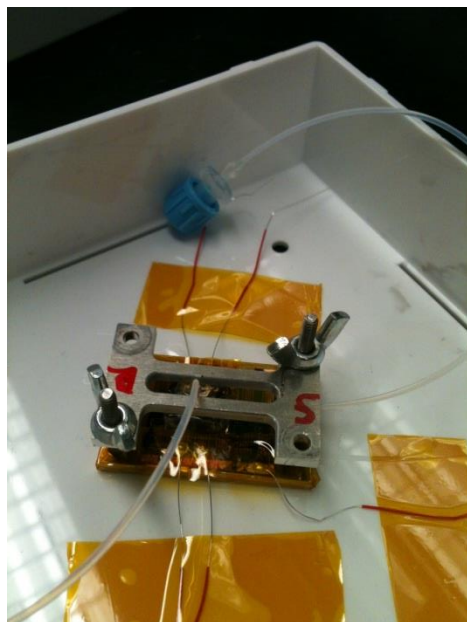
Supplementary Figure S2: Typical long-term stability of the fabricated polymer OFET. Despite being stored for one month in air, the transfer characteristics $I_{sd}(V_{bg})$ still shows remarkably high electronic performance (on/off ratio of $>10^2$ for the applied voltage range <10 V) and low hysteresis for multiple back-gate voltage sweeps.



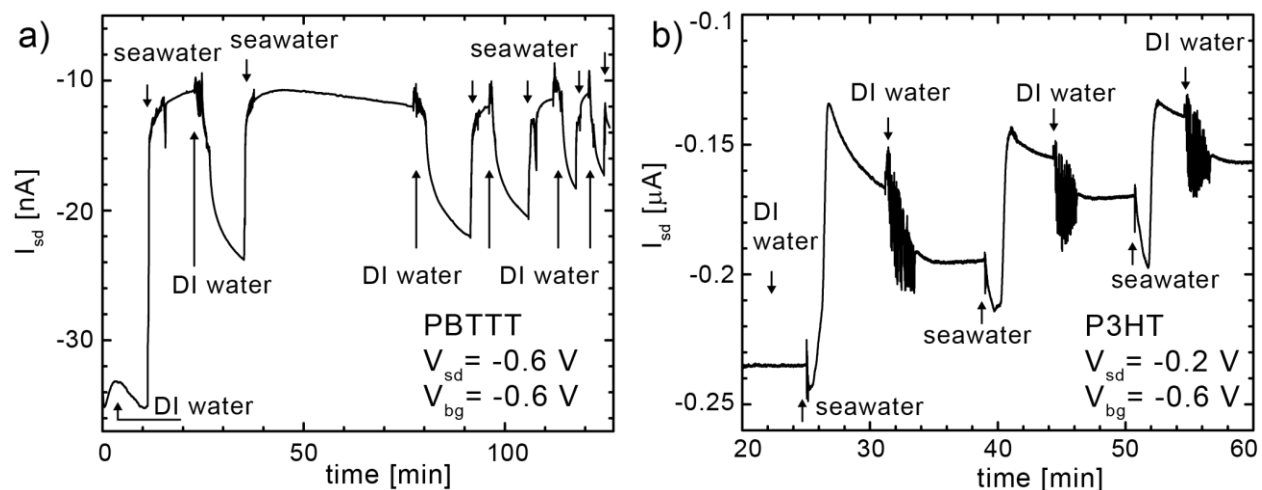
Supplementary Figure S3: Explanation of hysteresis observed for back-gated devices operated underwater. This behavior has been observed on two different dielectrics - on cross-linked PVP, shown here in **(a)** and on OTS treated SiO_2 in Fig.2c (see main manuscript). This behavior is potentially caused by the diffusion of ions through cracks in the spin-coated semiconductor thin film into the conductive channel or to the dielectric/polymer interface (top schematic shown in **(b)**, not to scale). These ions could potentially dope the semiconductor or form trap states and therefore interfere with the conductive channel at the dielectric/polymer interface, resulting in hysteresis.^{37,50} In the case of liquid-gating, the conductive channel is instead formed at the electrolyte/polymer interface (bottom schematic in **(b)**, not to scale). In this situation, the trap states at the dielectric/polymer interface would not interfere with the conductive channel, and no hysteresis is observed.



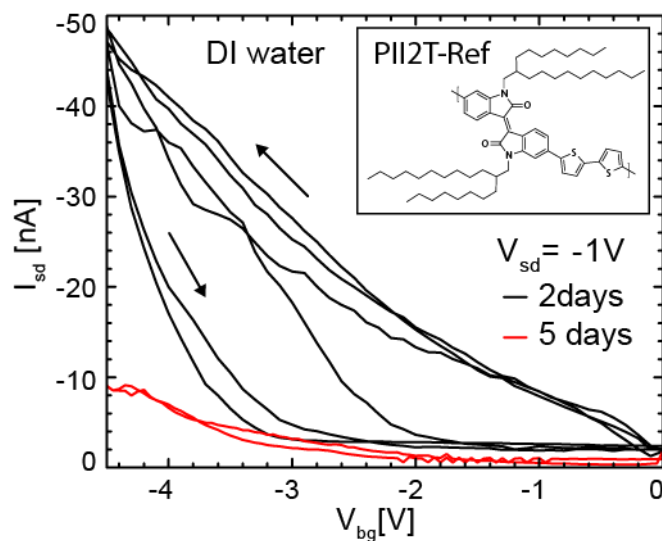
Supplementary Figure S4: Picture of the liquid-gating set-up. For liquid-gating experiments, a flow-through Ag/AgCl reference electrode was mounted in close vicinity to the flow cell and the OFET.



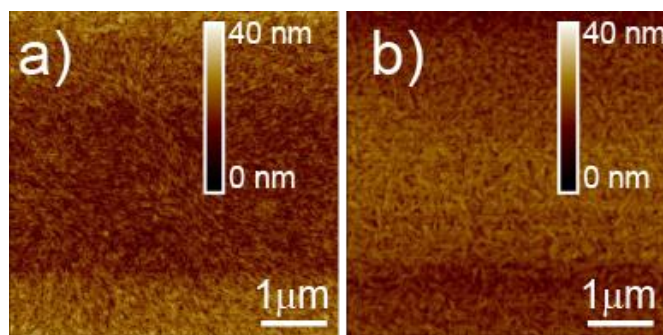
Supplementary Figure S5: Picture of the setup used for long-term stability testing of the polymer OFET in DI water and seawater. The mounted PDMS flow cell was filled with liquid and sealed to prevent evaporation of the liquid.



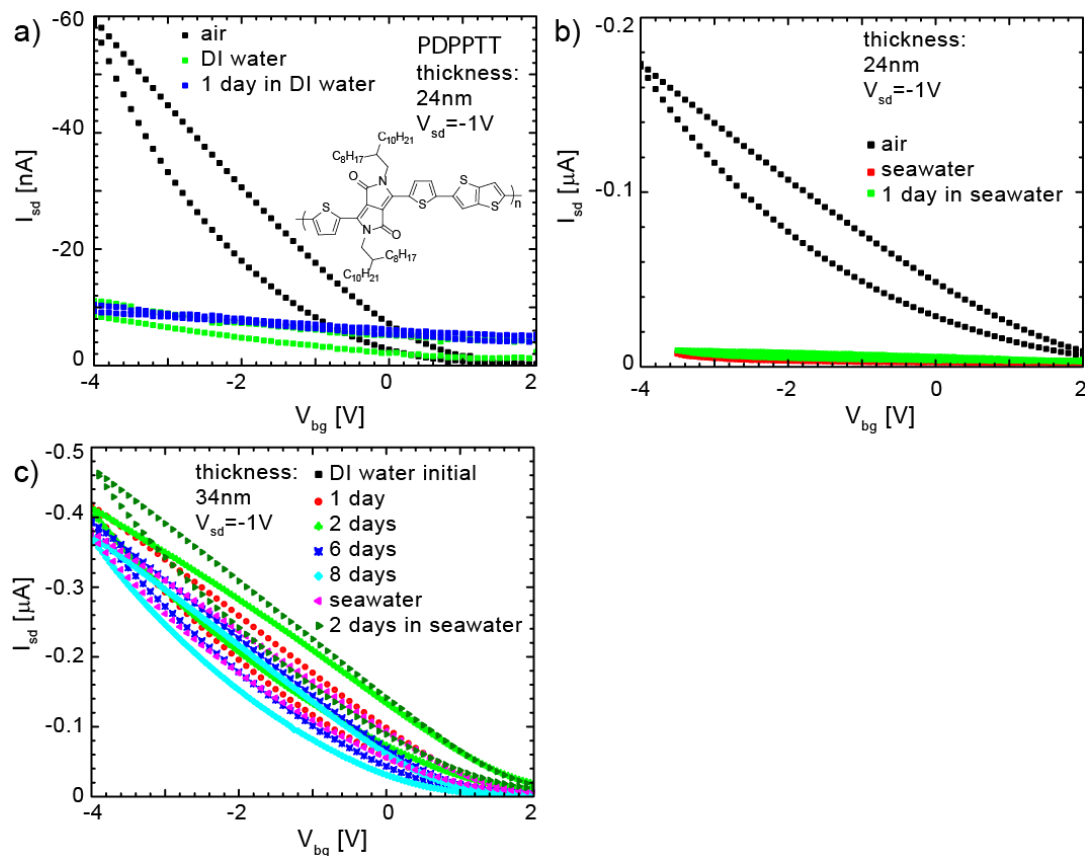
Supplementary Figure S6: Time resolved stability test (I_{sd} at fixed working point) for **(a)** PBTTT and **(b)** P3HT. A flow cell was mounted on these devices in the same fashion as the PII2T-Si devices and the device was alternately exposed to DI water and seawater. Both materials degrade almost immediately upon exposure to DI water and seawater. OFETs have been fabricated according to the same procedure described in the main manuscript.



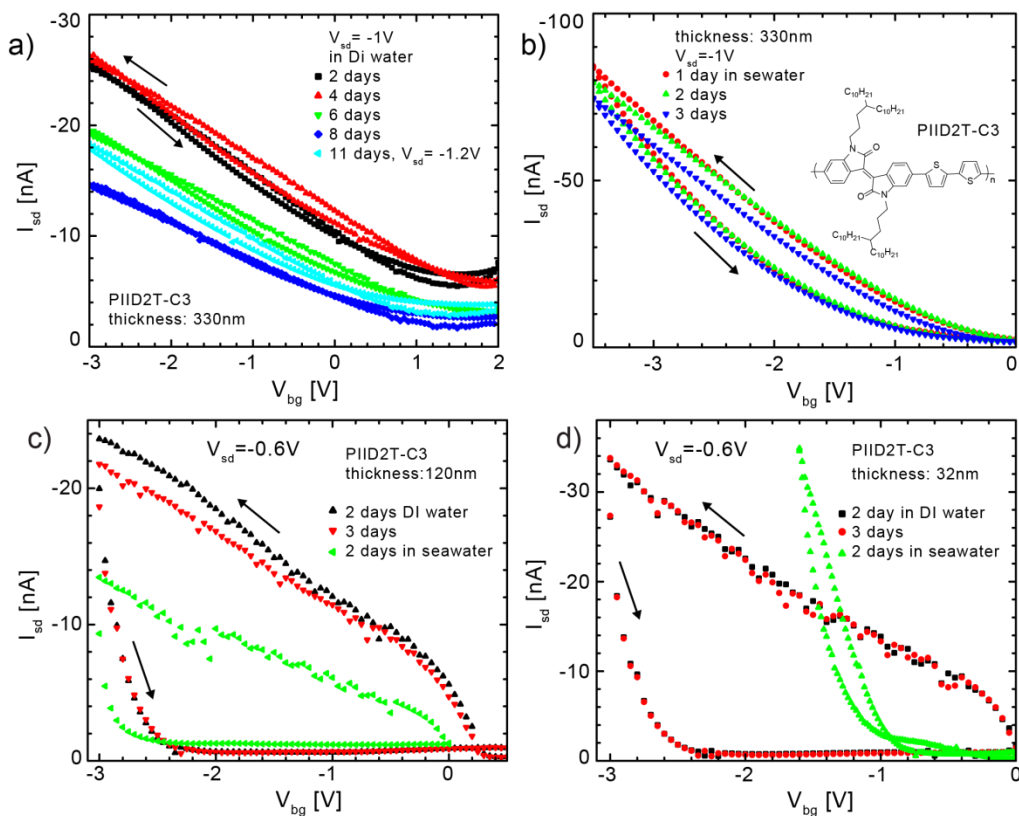
Supplementary Figure S7: In order to understand whether the water stability is a result of either the backbone or the siloxane side-chains, we performed stability tests with a reference polymer (PII2T-Ref) that contains branched alkyl side chains instead of the siloxane over several days.³³ We observe a dramatic decrease in device performance after a couple of days, and this decrease in performance for the PII2T-Ref devices were observed with multiple devices. From these observations, we conclude that the siloxane-chains play a role in stabilizing the OFETs. Additionally, the π - π stacking of the PII2T-Si polymer is more closely spaced (3.58 Å) than the PII2T-Ref polymer (3.76 Å).³³ The closer (tighter) packing may limit the penetration of water and oxygen molecules, therefore increasing the polymer's stability in aqueous environments.



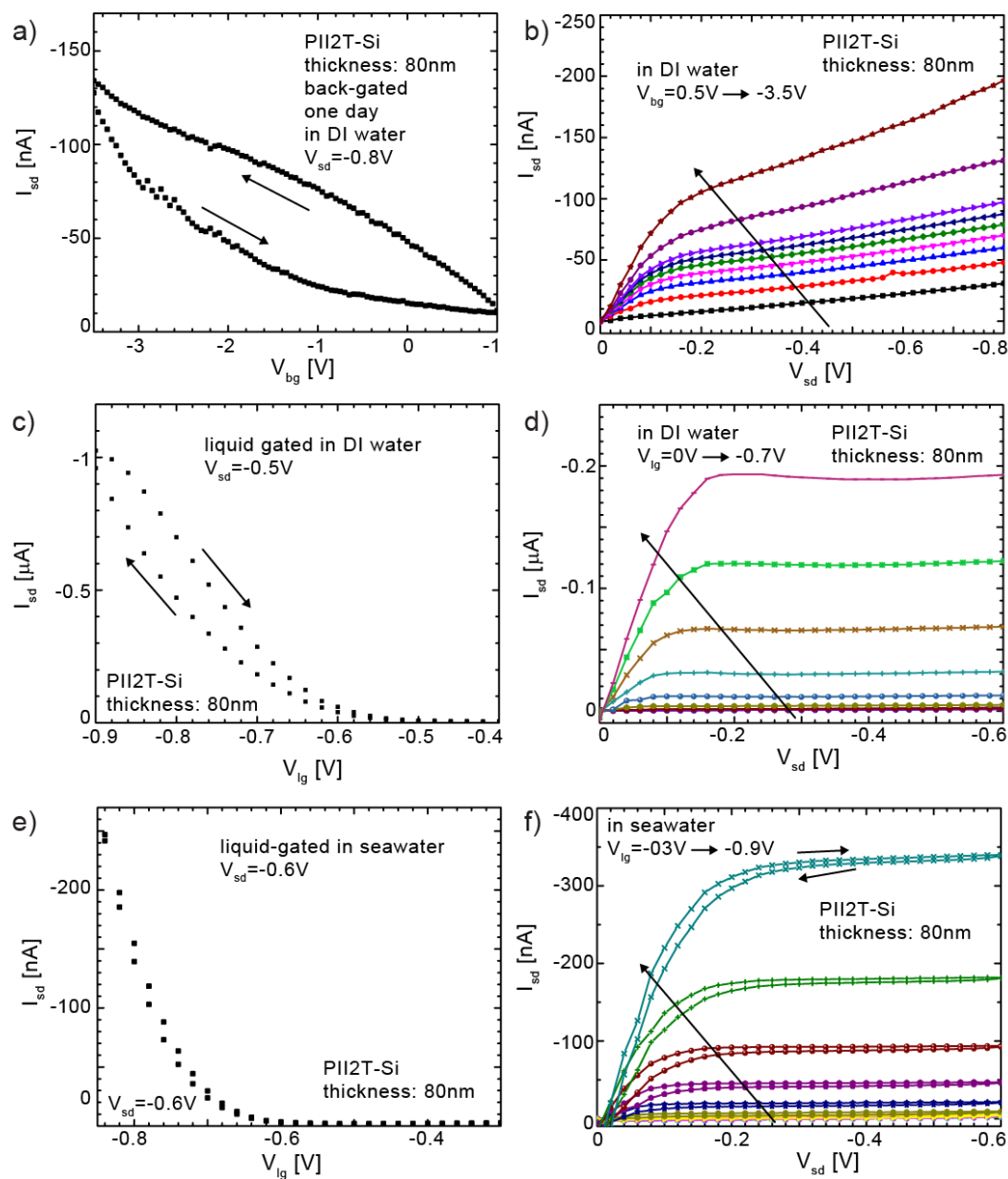
Supplementary Figure S8: Surface morphology of polymeric OFET devices fabricated using PII2T-Si **(a)** and PII2T-Ref **(b)**. The morphology of the surface is measured with an atomic force microscope operated in tapping mode. No significant differences in morphology are visible.



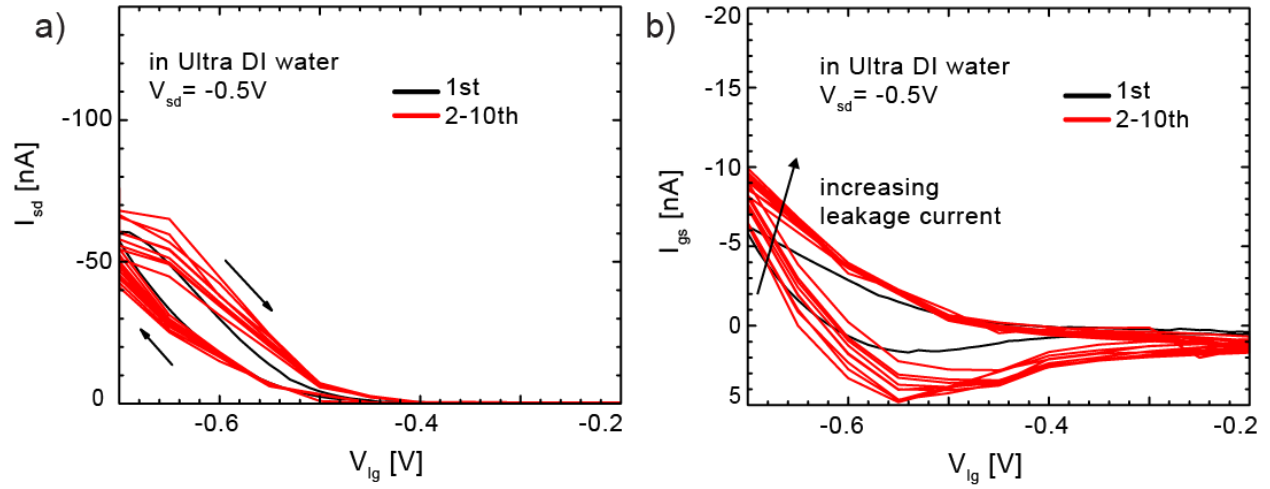
Supplementary Figure S9: To further understand whether the water stability is a result of the small π - π stacking, we performed stability tests with an air-stable PDPPTT based polymer⁴³ that has a small π - π stacking and similar energy levels compared to our PII2T-Si polymer. OFET sensors have been fabricated following literature procedures⁴³. We observed an instant decrease in device performance after direct exposure to DI water for a 24 nm thick film **(a)** and in seawater **(b)**. In **(c)** the performance of a double spin-coated polymeric layer is shown (thickness ~34 nm). In contrast, the performance is stable over multiple days in DI water as well as in seawater.



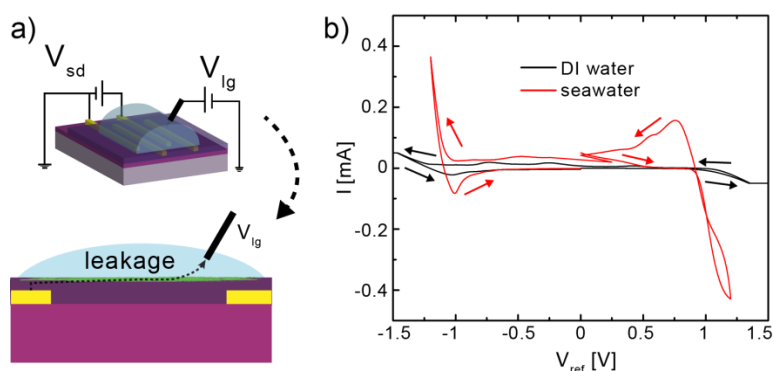
Supplementary Figure S10: Stability tests with an air-stable PIID2T-C3 based polymer⁴⁴ that has a small π - π stacking and similar energy levels compared to our PII2T-Si polymer. OFET sensors have been fabricated following literature values⁴⁴. The fabricated OFETs with a double spin-coated polymeric layer show stable electrical performance in DI water (a) and in seawater (b). Data collected from two different samples. In (c) the polymeric layer is ~120 nm thick. The OFET shows stable device performance in DI water. In seawater (green triangles) the performance is slightly decreases but the OFET is still operational. In (d) a polymeric OFET with a thinner single layer (~32nm) has been used. Stable device performance is observable in DI water. In seawater, we observe a slightly different performance but the device is still operational. Five samples have been measured for each thickness and the data shown are representative.



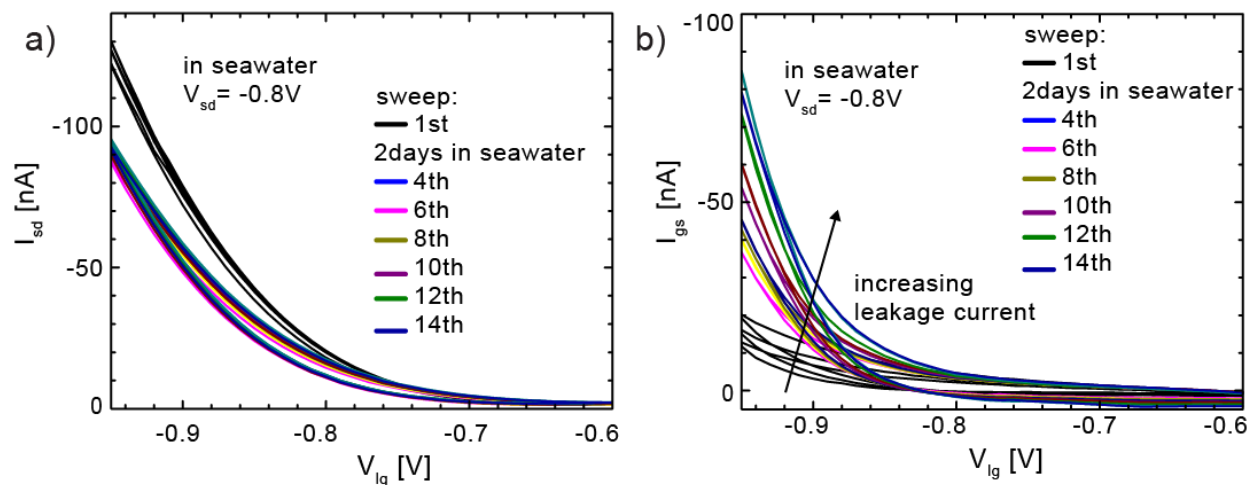
Supplementary Figure S11: Transfer and output characteristics of a single-layer (~80 nm thick) PII2T-Si OFET device. In (a) and (b) the device was kept one day in deionized water. We observe stable transfer (a) and output characteristic (b) and performance as measured with a two-layer device (see main manuscript Fig.2). The OFET was measured in a back-gate configuration in DI water. In (c) and (d) the same device is measured in a liquid-gate configuration. Again we observe similar device performance compared to a double-layer OFET device. In (e) and (f) a liquid-gate configuration was used to measure the electrical performance of a single layer device in seawater.



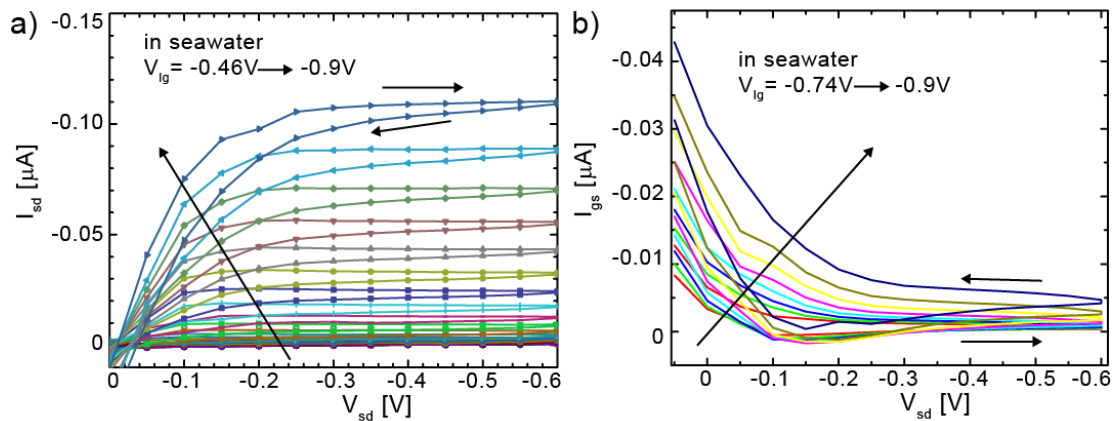
Supplementary Figure S12: Leakage current performance. **(a)** Transfer characteristics of I_{sd} vs. applied liquid-gate voltage V_{lg} in DI water monitored over multiple gate sweeps. The transfer characteristic remains constant over multiple gate sweeps. **(b)** Corresponding plot of gate-leakage current I_{gs} vs. applied liquid-gate voltage V_{lg} monitored over multiple gate sweeps. I_{gs} increases slowly (factor 2).



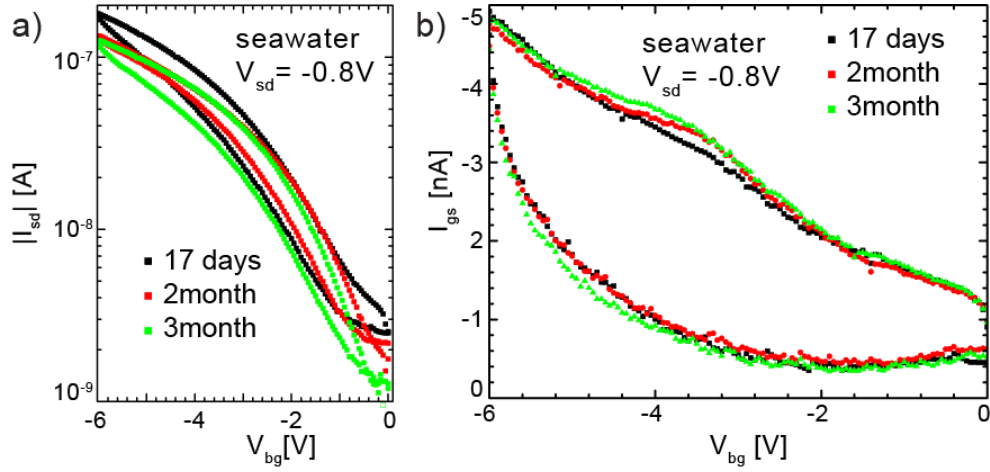
Supplementary Figure S13: Explanation of the leakage current behavior. **(a)** Schematic of the liquid-gate configuration (top). In this configuration, the conducting channel is formed at the OFET/electrolyte interface. Since no passivation layer protects the OFET, leakage currents are able to flow from the source-drain electrode through the conducting channel and into the liquid-gate electrode (bottom). The current that flows is a combination of an electronic (in the electrodes) and an ionic (in the electrolyte) current. It flows only when an appropriate electrochemical reaction occurs at the interface that allows an exchange of electrical charges between the electronic and the ionic media. **(b)** Measured voltammogram of the operation range of DI water and seawater. To avoid gate leakage, an electrolyte-gated OFET should be operated within the stability range of the electrolyte. In pure water, the stability range covers a little more than 1 V. In the presence of many ions, as it is the case in seawater we measured this range to be reduced to ~ 0.9 V, which may account for the additional leakage we observe in our experiments in seawater.



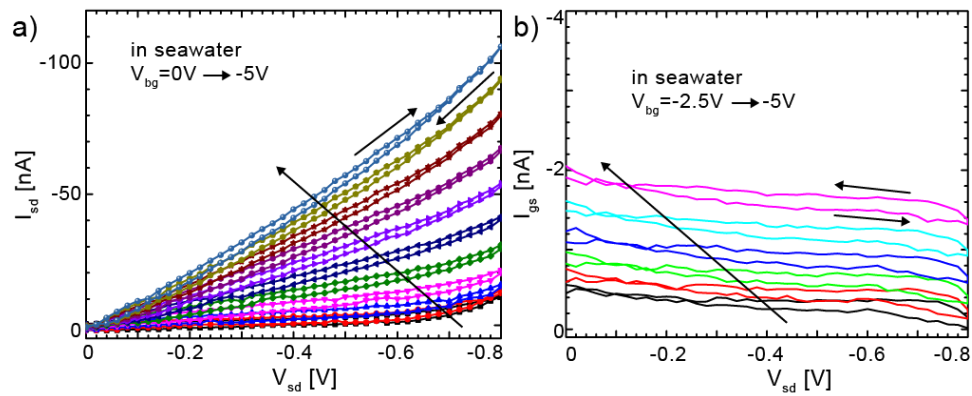
Supplementary Figure S14: Leakage currents in seawater. (a) Transfer characteristics of I_{sd} vs. applied liquid-gate voltage V_{lg} in seawater monitored over multiple gate sweeps and days. The transfer characteristic stabilizes and remains constant. Corresponding plot of gate-leakage current I_{gs} vs. applied liquid-gate voltage V_{lg} keeps increasing **(b)**. This effect is irreversible. The increase in I_{gs} is greater in magnitude (factor 5) compared to DI water due to the higher concentration of conducting ions present in seawater.



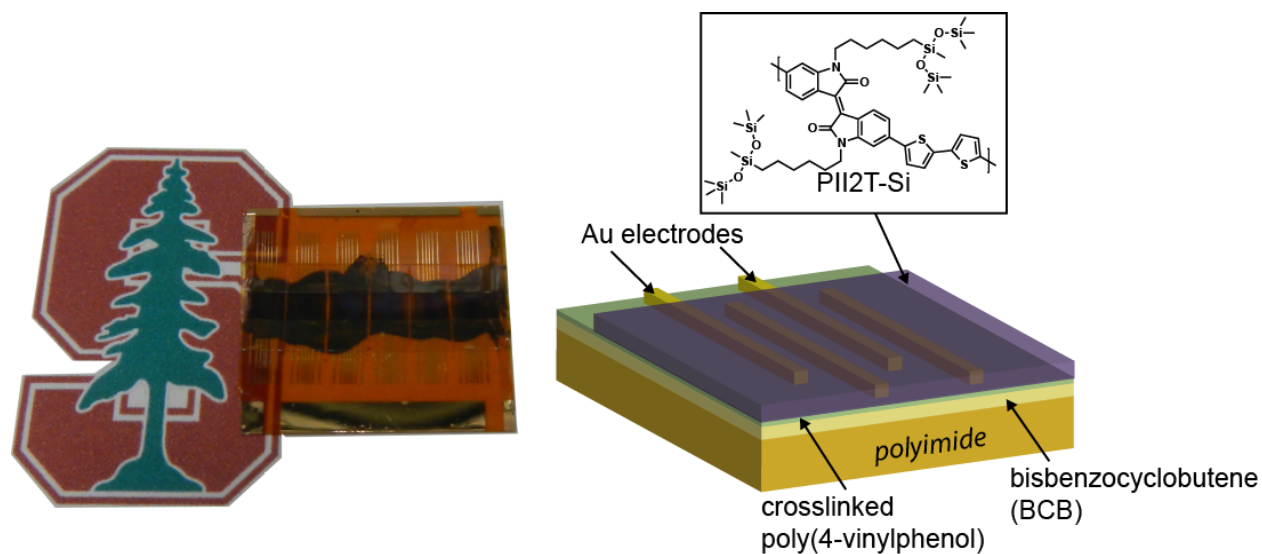
Supplementary Figure S15: Liquid-gated based leakage current in seawater. **(a)** Typical output characteristic (I_{sd} vs. V_{sd}) in forward and backward direction of a liquid-gated polymer OFET in seawater. A small hysteresis is visible which may point to the recombination of free charges from the channel with counter ions present in the liquid. This scenario is further reflected in an increased gate leakage current (I_{gs}) in the backward sweep, as shown in **(b)**.



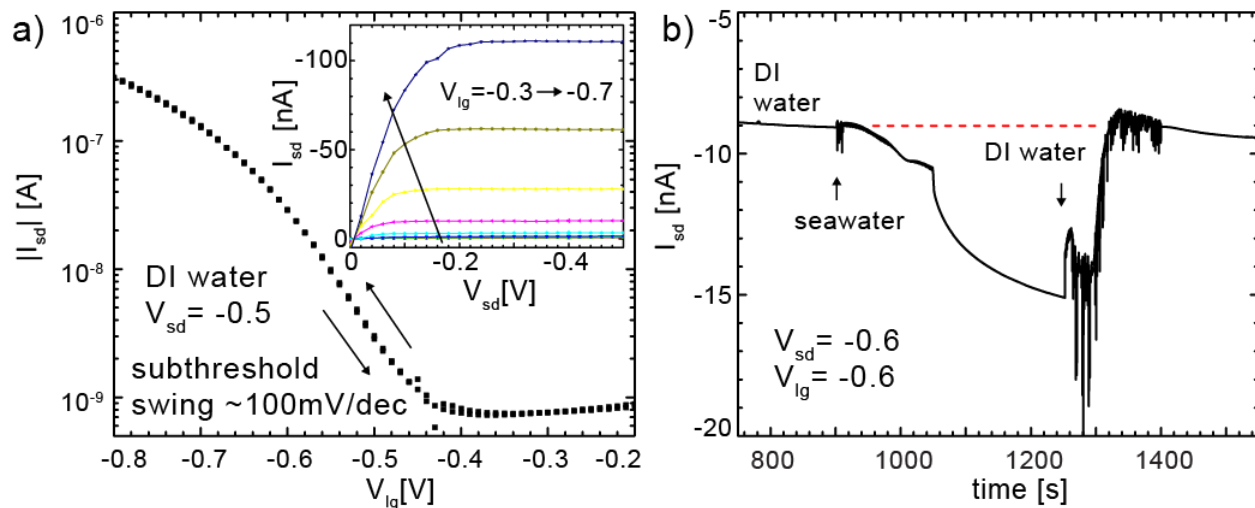
Supplementary Figure S16: Back-gated based leakage current in seawater. **(a)** Long term transfer characteristics of I_{sd} versus applied back-gate voltage V_{bg} in a semilogarithmic plot. The electrical performance of the OFET remains highly stable, even when stored in seawater for more than three months. **(b)** Gate leakage current I_{gs} vs. applied back-gate voltage in a linear plot. The leakage current remains constant over several months and more than 50 gate sweeps.



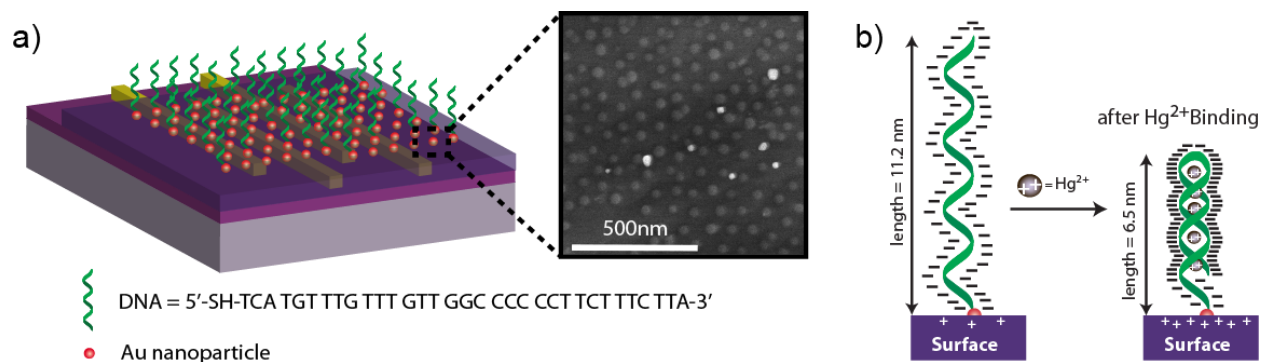
Supplementary Figure S17: Back-gated based leakage current in seawater. **(a)** Output characteristic (I_{sd} vs. V_{sd}) in forward and backward direction for different back-gate voltages V_{bg} in seawater. Only a small hysteresis is visible. **(b)** Corresponding gate-leakage current I_{gs} . The leakage remains almost constant during the backward sweep.



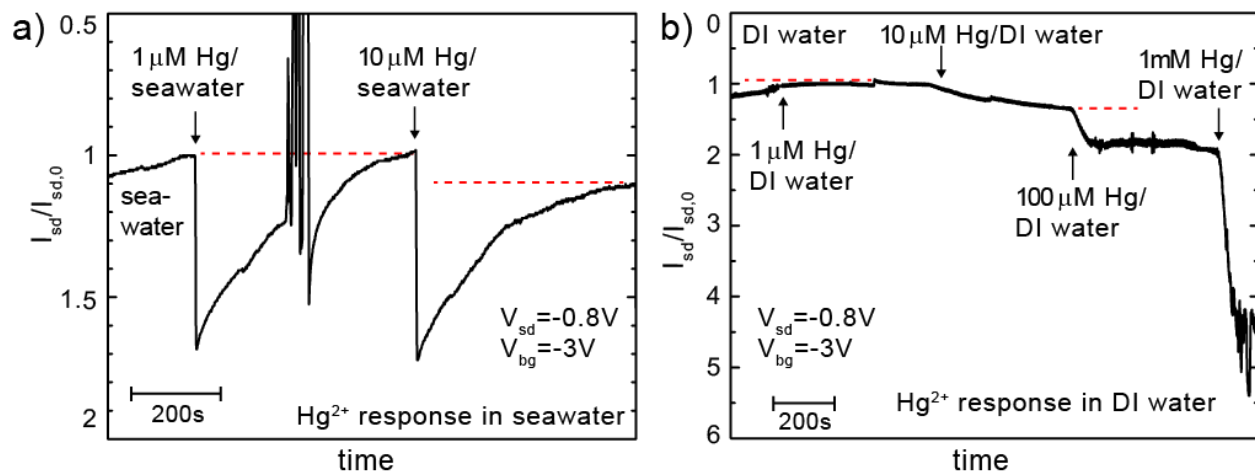
Supplementary Figure S18: Flexible OFET sensor. Optical image (left) and schematics of the fabricated OFET sensor (right) on a flexible polyimide substrate. A bisbenzocyclobutene (BCB) layer was deposited prior to the poly(4-vinylphenol) PVP dielectric layer to decrease the roughness of the polyimide. The flexible OFET sensors were operated in a liquid-gate configuration underwater.



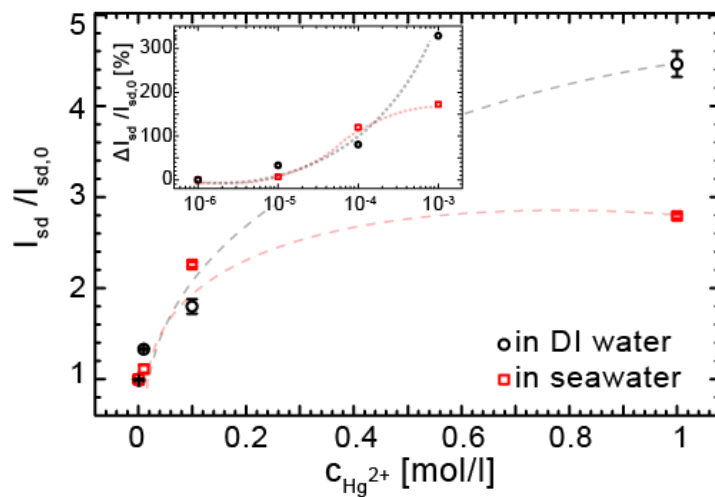
Supplementary Figure S19: Typical electronic properties of a liquid-gated flexible polymer OFET as shown in Supplementary Figure S18. **(a)** Transfer characteristics of I_{sd} vs. applied liquid-gate voltage V_{lg} in DI water is shown. The device shows excellent electronic performance with an absence of hysteresis, an on/off ratio $>10^2$ (for $\Delta V_{lg} < 400$ mV) and a subthreshold swing < 100 mV/dec. The output characteristics (I_{sd} vs. V_{sd}) are shown in the inset. **(b)** The flexible OFET is alternately exposed to DI water and seawater, in a similar fashion to Fig.3b in the main text. Upon introduction of seawater (~ 900 s), I_{sd} increases by a factor of ~ 2 . Switching back to DI water (~ 1290 s) decreases I_{sd} to the previously established baseline. The pump was turned off after the liquid volume in the flow-cell had been completely replaced (~ 1040 s and ~ 1400 s). The liquid-gated flexible OFET sensor confirms the trend previously observed in the non-flexible device for the increase in I_{sd} upon exposure to seawater.



Supplementary Figure S20: To demonstrate selective sensing, we spin-casted gold nanoparticles (AuNPs) onto the surface of the polymer OFET and attached a thiolated DNA aptamer that had previously reported specificity for Hg^{2+} .⁵² This specificity is a result of the thymine-thymine basepair mismatches in the sequence that are stabilized by incorporation of Hg^{2+} into the double helix.⁵² **(a)** Schematic of the selective OFET (not to scale) with a SEM image of the AuNPs (average spacing ~ 70 nm). Upon binding Hg^{2+} , the DNA undergoes a conformational change to form a hairpin structure,⁵⁷ as sketched in **(b)** (not to scale). This conformational change increases the density of the negative charges at the OFET's surface, inducing positive charges in the conductive channel of the polymer semiconductor according to the field-effect.²²



Supplementary Figure S21: In the main manuscript we showed the selective detection of Hg^{2+} ions at 1 mM concentration. We also studied the detection limit of our selective OFET sensor with the AuNP functionalization (average spacing ~ 80 nm). In (a) the time resolved response of I_{sd} at constant V_{sd} and V_{bg} is shown upon introduction of different concentrations of Hg^{2+} ions dissolved in seawater. The OFET responses show a change in I_{sd} and establishment of a stable current plateau for a concentration down to $10 \mu M$ (red dashed lines). No I_{sd} change is visible for lower concentrations. In (b) the same experiment has been repeated but for Hg^{2+} ions dissolved in DI water. Similarly, we can detect Hg^{2+} ions down to a concentration of $10 \mu M$ (red dashed lines). We find that the background ionic strength of seawater does not screen the OFET's response to Hg^{2+} ions. Though it was beyond the scope of this manuscript, the detection limit of our OFET sensor may be enhanced by a closer packing of the AuNPs.



Supplementary Figure S22: Normalized source-drain current change ($I_{sd}/I_{sd,0}$) vs. Hg^{2+} ion concentration. Measurements were performed in DI water (black circles) and seawater (red squares). The inset shows the sensitivity on a semi-logarithmic scale. Dashed lines are guides to the eye. The magnitude of the OFET's response to Hg^{2+} ion is decreased in seawater as compared to DI water. This effect may be due to screening effect of the background ion concentration of seawater.

	V_{th} [V]	μ [cm^2/Vs]	on/off		V_{th} [V]	μ [cm^2/Vs]	on/off
Back-gated, in ambient:	on PVP: -0.74±0.04 on SiO ₂ /OTS: -3.13±0.24	overall: 0.017±0.009	overall >100				
Liquid-gated				Back-gated			
liquid used:				liquid used:			
in 10 μM NaCl	-0.72±0.02	0.0014±0.0008	>150	in DI water	-1.62±1.25	0.035±0.02	>130
In seawater	-0.75±0.01	0.005±0.003	>380	in seawater	-1.89±1.25	0.01±0.004	>150
In DI water	-0.73±0.07	0.004±0.003	>650				

Supplementary Table S1: Electrical figures of merit at low voltages in ambient and in different solutions averaged over at least four different OFETs (threshold voltage (V_{th}), electrical mobility (μ) and on/off ratio) for the liquid-gate (left) and back-gate configuration (right).

Polymer	Layers	Thickness (nm)	π - π stacking	Packing	Contact angle	stable DI water	stable SW	E _{homo} [V]	E _{lumo} [V]
PII2T-SI (4mg/ml)	1	~80	3.58	mix	102°	yes	yes	-5.2	-3.59
PII2T-SI (4mg/ml)	2	~132	3.58	mix	102°	yes	yes	-5.2	-3.59
PII2T-Ref (4mg/ml)	2	~130	3.75	edge on	105°	no	no	-5.38	-3.76
PDPPTT (5mg/ml) ref. ⁵	2	~34	3.43	edge on	97.5°	yes	yes	-5.2	-3.5
PDPPTT (5mg/ml)	1	~24	3.43	edge on	97.5°	no	no	-5.2	-3.5
PIID2T-C3 (4mg/ml) ref. ⁶	2	~330	3.57	edge on	95.2°	yes	yes	-5.52	-3.74
PIID2T-C3 (4mg/ml)	1	~120	3.57	edge on	95.2°	yes	yes	-5.52	-3.74
PIID2T-C3 (2mg/ml)	1	~32	3.57	edge on	95.2°	yes	yes	-5.52	-3.74

Supplementary Table S2: Summary of the measured polymers with their different properties.

	V_{th} [V]	μ [cm ² /Vs]	$\Delta V_{th}/day$ [mV]
Back-gated			
Seawater with AuNP	-1.14	0.012	6
Seawater with AuNP	-1.57	0.009	16

Supplementary Table S3: Electrical figures of merit (threshold voltage V_{th} , electrical mobility μ , average threshold voltage shift ΔV_{th}) for two gold nanoparticle decorated polymeric OFET devices in a back-gate configuration after 11 days in seawater.

Method	System	Detection limit (nM)	Reference
Optical	Gold nanoparticles	100	Lee et al. (⁵⁸)
Optical	Quantum dots	~0.8	Ma et al. (⁵⁹)
Electrical readout	Carbon nanotube FETs	10	Kim et al. (⁶⁰)
Electrical readout	Graphene oxide FETs	1200	Sharon et al. (⁶¹)
Electrical readout	n-type single molecule OFETs	50000	Ramesh et al. (⁶²)
Electrical readout	Polymeric OFET	10000	This study

Supplementary Table S4: Analysis of different Hg²⁺ sensing platforms.

Supplementary Note 1. Electrical figures of merit

We calculated the average mobility of the devices using the back-gate capacitance of 11 nF/cm^2 (ref.³³) and an average liquid-gate capacitance of $10\mu\text{F/cm}^2$ (ref.⁶³). The mobility in the liquid-gated configuration was lower than that in the back-gated configuration. A similar finding has been previously reported for electrolyte-gated OFETs,³⁷ and can be explained by the increased gate dielectric capacitance (in this case, the electrical double layer) which tends to confine charge carrier distribution at the electrolyte/OFET interface. Hence, the charge transport is more sensitive to surface roughness and interface defects for the liquid-gated sample.

Supplementary Note 2. Potential explanation of the water stability

Even though both polymer surfaces (PII2T-Si and PII2T-Ref) were hydrophobic with contact angles $>95^\circ$ (Supplementary Table S2), the PII2T-ref polymer with a greater thickness ($\sim 130\text{ nm}$) and a larger π - π stacking distance ($3.76\text{ \AA}$) compared to PII2T-Si with a lower thickness ($\sim 80\text{ nm}$) and a lower π - π stacking distance ($3.58\text{ \AA}$) is not stable. Therefore for a better comparison, we studied the stability of two additional polymeric semiconductors which are known to be highly air-stable. The first one is a PDPPTT-based conjugated polymer which was reported to be highly stable in air.⁴³ Further we used PIID2T-C3, an isoindigo-based polymer which is also known to be highly air stable.⁴⁴ We fabricated polymeric OFET devices following the same fabrication protocol described in the method section of the manuscript, while using optimized parameters taken from the literature.^{43,44} The PDPPTT and PIID2T-C3 polymers were selected due to their similarities to PII2T, in addition to their air stability. Both have a small π - π stacking ($<3.6\text{ \AA}$) as well as similar energy levels. Recently, it has been shown that a small π - π stacking may be the reason for air stability.⁴⁵ In our studies, we found that this argument may be valid for the stability in liquid environments as well. Similar to our PII2T-Si polymer, these two additional polymers were stable in aqueous environments. This is in contrast to the PII2T reference polymer, which has a larger π - π stacking ($3.76\text{ \AA}$). Additionally, we found that the thickness of the polymer layer may also be responsible for the stability in aqueous environments. To fabricate OFET sensors, we typically spin-coated one or two layers of polymer (see methods section, main manuscript). We found that while our PII2T-Si polymer is stable for a single layer ($\sim 80\text{ nm}$, Supplementary Figure S11 and Supplementary Table S2) as well as the double layer ($\sim 130\text{ nm}$), PDPPTT's stability is thickness dependent. A single spin-coated layer ($\sim 20\text{ nm}$) is not stable in an aqueous media (Supplementary Figures S9a and 9b) though a double

spin-coated OFET (~35 nm) is stable (Supplementary Figure S9c) in deionized and seawater. A double layer of the PII2T-C3 polymer is very thick (~330 nm), compared to the two other polymers and shows stable characteristic in deionized water as well as in seawater (Supplementary Figures S10a and 10b). As a single layer (~120 nm), the performance is also stable in contact with an aqueous solution (Supplementary Figure S10c). In order to achieve a comparable single-layer thickness to the other polymers, we further diluted this polymer and the spin-casted film (~32nm). The fabricated OFETs are still stable (Supplementary Figure S10d) although slightly changing their electrical characteristic in contact with seawater. This result indicates that there may be a thickness-based threshold (in our case ~30 nm), above which these polymers with small π - π stacking are stable. All polymers show a high contact angle (> 95°) and are highly hydrophobic. Our findings are summarized in Supplementary Table S2.

Supplementary Note 3. Back-gated OFET performance in aqueous environments

Testing OFETs in a back-gate configuration and in saturation range may be achieved by using thinner high quality dielectric layers. We tested our PII2T-Si polymer performance on a cross-linked PVP dielectric layer with a thickness of ~80nm (method section, main manuscript).⁶⁴ However, PVP has a low breakdown voltage range⁶⁴ and only small back-gate voltages can be applied. For that reason and to reduce the leakage current to the back-gate, we performed stability tests on SiO₂. There have been recent developments in new dielectric materials for low-voltage operation.^{65,66,67} Future work will be done to reduce leakage current in thin dielectric layers for underwater operations.

Supplementary Note 4. Mechanism for selective sensing of Hg²⁺ ions and detection limit

The mechanism by which the DNA binds the Hg²⁺ results in a conformational change of the DNA in which the DNA forms a hairpin structure by self-hybridizing around the Hg²⁺ ions (Supplementary Figure S20b).⁵³ This effect originates from the thymine-thymine mismatch stabilization due to the incorporation of Hg²⁺ (ref. ⁵⁷). While up to 7 Hg²⁺ ions (each with +2 charge) are bound by each DNA,⁵³ the self-hybridization of the DNA brings 14 base pairs (each with -2 charge) in closer proximity to the surface of the OFET. Because of the conformational change in the DNA, the negative charge density is increased on

the surface of the semiconductor. This will induce positive charges in the semiconductor⁶⁸ and was previously observed with the adsorption of DNA onto an OFET.²² We extracted and plotted the normalized average response $I_{sd}/I_{sd,0}$ of our polymeric OFET sensor to different Hg^{2+} concentrations in DI water and seawater (Supplementary Figure S22). Data has been collected from three different samples. Dashed lines are guides to the eyes. The response in DI water is larger compared to the response in seawater. This effect may be related to screening effects from the background ions in seawater.⁵⁴

Supplementary References

57. Miyake Y. et al. MercuryII-Mediated Formation of Thymine–HgII–Thymine Base Pairs in DNA Duplexes. *Journal of the American Chemical Society* **128**, 2172–2173 (2006).
58. Lee, J.-S., Han, M. S. & Mirkin, C. Colorimetric detection of mercuric ion (Hg²⁺) in aqueous media using DNA-functionalized gold nanoparticles. *Angewandte Chemie* **46**, 4093–4096 (2007).
59. Ma, J., Chen, Y., Hou, Z., Jiang, W. & Wang, L. Selective and sensitive mercuric (ii) ion detection based on quantum dots and nicking endonuclease assisted signal amplification. *Biosensors & Bioelectronics* **43**, 84–87 (2013).
60. Kim, T. H., Lee, J. & Hong, S. Highly Selective Environmental Nanosensors Based on Anomalous Response of Carbon Nanotube Conductance to Mercury Ions. *The Journal of Physical Chemistry C* **113**, 19393–19396 (2009).
61. Sharon, E., Liu, X., Freeman, R., Yehezkeli, O. & Willner, I. Label-Free Analysis of Thrombin or Hg²⁺ Ions by Nucleic Acid-Functionalized Graphene Oxide Matrices Assembled on Field-Effect Transistors. *Electroanalysis* **25**, 851–856 (2013).
62. Ramesh, M., Lin, H.-C. & Chu, C.-W. Organic thin film transistors as selective sensing platforms for Hg²⁺ ions and the amino acid cysteine. *Biosensors & Bioelectronics* **42**, 76–9 (2013).
63. Magliulo, M. et al. Electrolyte-Gated Organic Field-Effect Transistor Sensors Based on Supported Biotinylated Phospholipid Bilayer. *Advanced Materials* **25**, 2090-2094 (2013).
64. Roberts, M. E., Mannsfeld, S. C. B., Reinecke, B. N., Knoll, W. & Bao, Z. Cross-Linked Polymer Gate Dielectric Films for Low-Voltage Organic Transistors. *Chemistry of Materials* **20**, 2292–2299 (2009).
65. Ponce Ortiz, R., Facchetti, A. & Marks, T. J. High-k organic, inorganic, and hybrid dielectrics for low-voltage organic field-effect transistors. *Chemical Reviews* **110**, 205–39 (2010).
66. Halik, M. et al. Low-voltage organic transistors with an amorphous molecular gate dielectric. *Nature* **431**, 963–966 (2004).
67. Herlogsson, L. et al. Low-Voltage Polymer Field-Effect Transistors Gated via a Proton Conductor. *Advanced Materials* **19**, 97–101 (2007).
68. Capua, E., Natan, A., Kronik, L. & Naaman, R. The molecularly controlled semiconductor resistor: how does it work? *ACS Applied Materials & Interfaces* **1**, 2679–2683 (2009).