Mercury-mediated organic semiconductor surface doping monitored by electrolyte gated field effect transistors

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Surface doping allows tuning the electronic structure of semiconductors at near-surface regime and is normally accomplished through the deposition of an ultrathin layer on top or below the host material. Surface doping is particularly appealing in organic field-effect transistors (OFETs) where charge transport takes place at the first monolayers close to the dielectric surface. However, due to fabrication restrictions that OFET architecture imparts, this is extremely challenging. Here, we demonstrate that mercury cations, Hg^{2+} , can be exploited to control doping levels at the top surface of a thin film of a p-type organic semiconductor (OSC) blended with polystyrene. Electrolyte- or water-gated field-effect transistors (EGOFETs or WGOFETs), which have its conductive channel at the top surface of the organic thin film, turn out to be a powerful tool for monitoring the process. A positive shift of the threshold voltage is observed in the devices upon Hg^{2+} exposure. Remarkably, this interaction has been proved to be specific to Hg^{2+} with respect to other divalent cations and sensitive down to nanomolar concentrations. Hence, this work also opens new perspectives for employing organic electronic transducers in portable sensors for the detection of an extremely harmful water pollutant without the need of using specific receptors.

1. Introduction

Organic electronics represent one of the most straightforward route towards flexible devices due to the low temperature fabrication processes involved and, thus, compatibility with polymeric substrates. Additionally, organic semiconductors (OSCs) are appealing for their versatile modulation, since materials can be produced *à la carte* by chemical synthesis. Furthermore, a viable way to achieve fine-control of the electronic properties of organic semiconductors is by chemical doping, which consists in adding an impurity able to donate (*i.e.*, n-doping) or accept (*i.e.*, p-doping) an electron to or from the semiconductor, respectively.^[1] Doping typically gives rise to an increase of the OSC conductivity or a reduction of the contact resistance between the organic semiconductor and the metal electrodes.^[1–4] In general, doping can be achieved either by: i) processing simultaneously the dopant and semiconductor either by the co-evaporation of both materials,^[5] or by employing wet-processes (*i.e.* spin-coating) of a solution containing the doping agent and the organic material,^[6] or ii) exposing the semiconductor thin film to vapors of the dopant.^[7] Up to now, doping techniques are successfully applied in organic optoelectronics for a broad commercial products, such as in highly efficient white organic light-emitting diode or organic solar cell.^[8,9]

Chemical doping of the OSC has also been exploited in organic field-effect transistors (OFETs).^[10,11] However, since in these devices charge transport takes place only at the first monolayers close to the dielectric surface,^[12] it is, therefore, extremely desirable to achieve a controlled doping of such interface. Unfortunately, this is extremely challenging due to restrictions that OFET architecture imparts on fabrication. A reliable way to dope locally the surface of OSC thin films includes the use of self-assembled monolayers (SAMs) sandwiched between the OSC and dielectric surface^[13–15] or the deposition of a doping layer of a strong electron-withdrawing (or electron-donating) molecule on top of a few monolayer-thick OSC.^[16] A particular class of OFET devices are the so-called electrolyte-gated or water-gated

organic field-effect transistors (EGOFETs or WGOFETs), in which a water saline solution or simply water is used as gating medium.^[17] These devices are recently gaining much attention because of their potential in biochemical sensing applications. The conduction channel in WGOFETs is formed at the OSC/water interface and, hence, these devices offer a unique, but completely unexplored, opportunity to be subjected to surface transfer doping by adding the appropriate dopant in the aqueous medium.

In this paper, we report a mercury-mediated surface doping of a thin film of a p-type OSC blended with polystyrene (PS) induced by a redox reaction between an aqueous mercury solution (HgCl_2) and the OSC. It has been previously shown that the films prepared by these OSC/PS blends are self-encapsulated by the polymer and, hence, a poor permeation of the ions into the OSC is expected.^[18,19] In order to monitor the doping level, we have exploited the WGOFET layout as electronic transducer. The devices were systematically exposed to reference solutions of Hg^{2+} , thereby affecting its surface electrical characteristics due to the redox reaction between this divalent cation and the organic semiconductor. Remarkably, this interaction has been proved to be specific to Hg^{2+} with respect to other divalent cations and sensitive down to nanomolar concentration. This is of paramount interest since the development of portable and low-cost sensors to detect Hg^{2+} in waters represents one of the most compelling issues identified by the EEA (European Environmental Agency) and WHO (World Health Organization) due to its high toxicity. Considering all above, the importance of the herein reported results is two-fold: i) a new approach for surface doping of OSCs is established by making use of the WGOFETs configuration, and ii) a novel and simple organic sensing platform towards the extremely harmful pollutant Hg^{2+} is demonstrated without the need of using specific receptors or complex device architectures.

2. Results and Discussion

We previously demonstrated that the use of OSCs blended with polystyrene (PS) and deposited by bar-assisted meniscus shearing (BAMS) gives rise to highly crystalline and homogenous thin-films that exhibit excellent OFET performance.^[18,20,21] One additional advantage of this strategy is that the thin-films are self-encapsulated by a thin PS protecting layer, which combined with the high OSC crystallinity, provides the devices a high environmental stability. Thus, these films have also shown to reveal robust electrical performances as WGOFETs, exhibiting high mobility and fast switching speed.^[19,22] Here, we selected as OSC 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TES-ADT, **Figure 1a**), which was blended with PS in a ratio (4:1) and dissolved in chlorobenzene (2 % wt.). Films were prepared by BAMS at 105 °C and deposited at 1 cm/s as previously reported.^[20]

As shown in Figure 1b, the electrical measurement setup consists in a polydimethylsiloxane (PDMS) pool mounted on top of the device with a Pt wire acting as gate electrode. Prior to exposing the device to the Hg^{2+} solution, a stability check in MilliQ water was always performed in order to guarantee a reproducible electrical response (*i.e.* few I - V transfer characteristics are recorded). As displayed in Figure S1a (Supporting Information), the perfect overlapping of the transfer scans ensures that the WGOFET response is stable and no electrical deterioration is occurring in the experimental time-scale. Transfer and output characteristics (Figure S1c, Supporting Information) show a typical p-type behavior in a V_{GS} windows ranging from +700 to -300 mV. These devices exhibited average hole mobility and threshold voltage of $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 0.4 V, respectively (Table S1).

Then, in order to test the sensitivity of the OSC towards Hg^{2+} , we systematically exposed the OSC thin film to increasing concentrations of HgCl_2 by spanning 6 orders of magnitude, namely from nanomolar to millimolar levels (*i.e.* 1 nM, 50 nM, 1 μM , 50 μM and 1 mM). The detection setup is sketched in Figure 1c. A droplet of the solution containing HgCl_2 was

casted on the interdigitated area for three minutes followed by an abundant washing of the surface with MilliQ water for removing traces of this salt solution that could interfere with the water-gated measurements. After mercury exposure, we performed an additional stability check in MilliQ water in order to ensure again the stability and reproducibility of the data (see Figure 1d and Figure S1b, Supporting Information). Clearly, electrical performances are affected after the Hg^{2+} exposure, as a result of the marked threshold voltage (V_{th}) shift. As evidenced in Figure 1e, a positive V_{th} shift is observed with increasing the Hg^{2+} concentration. This gradual shift is accompanied by an increase of the off-current (I_{off}) and on-current (I_{on}) (see Figure S2a, Supporting Information). These trends are characteristic of a p-doping process of the organic semiconductor.^[16] Figure S2b (Supporting Information) clearly shows the best overlap of all the transfer curves of a device exposed to solutions of Hg^{2+} at variable concentration compared to the same device measured without ion exposure. This can be achieved by simply shifting the curves along the V_{GS} axis according to: ($V_{GS}^{eff} = V_{GS} - V_{th}$). The excellent overlap of all these transfer curves suggests that V_{th} is the most affected parameter among the multi-parametric response offered by a field-effect transistor.

Aiming at quantifying the V_{th} dependency with respect to Hg^{2+} concentration, we have extracted this parameter according to the classical MOSFET equation in saturation regime:

$$I_{DS} = \frac{W}{2L} C_{dl} \mu_{FET} (V_{GS} - V_{th})^2 \quad (1)$$

where μ_{FET} is the charge-carriers mobility, W is the channel width, L is the channel length, V_{th} the threshold voltage, V_{GS} is gate-source voltage and C_{dl} is the capacitance of the electrical double layer.^[22] The constant slopes of $\sqrt{I_{DS}}$ vs. V_{GS} (Figure S2c and Table S1, Supporting Information) indicate that the following product, $\mu_{FET} \cdot C_{dl}$ (in accumulation regime), are not significantly affected by Hg^{2+} exposure.^[23] Figure 1f shows that a linear relationship exists between ΔV_{th} and the $\log [\text{Hg}^{2+}]$, defined as $\Delta V_{th} = V_{th}^{\text{Hg}^{2+}} - V_{th}^{\text{MilliQ water}}$, within the selected range from 1 nM to 1 mM. The linear dependence suggests that the sensitivity of the

device, defined as the slope of the curve, is equal to 27 ± 10 mV/dec. These data were extracted from 10 devices (Table S2, Supporting Information), whose statistical results are also plotted in Figure S2d (Supporting Information). All the positive ΔV_{th} indicates that a higher gate voltage is required to switch the channel off due to the p-doping effect of Hg^{2+} .^[24] From the transfer characteristics in linear regime (see Figure S3a, Supporting Information), we have extracted the carriers concentration (n) induced by the gate voltage V_G according to the following equation:^[25]

$$n = -\frac{C_{dl}(V_{GS}-V_{th})}{e} \quad (2)$$

here e is the elementary charge. The doping-induced hole concentration estimated by $\Delta n_{doping} = n^{Hg^{2+}} - n^{initial}$, at $V_{GS} = -0.1$ V in accumulation regime, is plotted with respect to different Hg^{2+} concentrations in Figure S3b (Supporting Information). A gradual increase of carriers concentration induced by the Hg^{2+} -mediated surface doping has been achieved. In fact, devices which have not been exposed to Hg^{2+} have hole concentrations of 4.7×10^{11} carriers·cm⁻², but this value increases up to 4.9×10^{12} carriers·cm⁻² ($V_{GS} = -0.1$ V) after mercury exposure ($c = 1$ mM). In other terms, the surface doping raises up to one order of magnitude the charge carrier concentration.

We have systematically tested the effect of 1 mM solutions of a wide range of divalent metal cations, such as Zn^{2+} , Mg^{2+} , Mn^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} and Pb^{2+} in order to gain insights on the mechanism that governs the above-mentioned surface doping. As reported in **Figure 2a** and Figure S4 (Supporting Information), all the transfer characteristics only show a small negative shift of V_{th} when the devices are exposed to these cations, which is normally observed within the experimental error. This suggests a negligible interaction between the OSC and these possible interfering cations. Within this context, mixed solutions containing different divalent cations have been prepared by keeping the same final concentration (*i.e.* 1 mM) in order to test the WGOFET response in a more complex media. As a result, it was

found that the devices show a clear positive potentiometric shift only in presence of Hg^{2+} (see Figure 2b-d and Figure S5, Supporting Information), whereas no change or a slightly negative V_{th} shift is observed when Hg^{2+} cations are absent. All these results confirm that a preferential interaction with Hg^{2+} cations is occurring with respect to all the other divalent cations.

In order to get deeper insights into the interaction mechanism between Hg^{2+} and the electronic transducer, we have performed a series of cross-checks. First, to rule out a possible partial diffusion of Hg^{2+} cations towards the underlying Au contacts (*viz.* source and drain electrode), we carried out an electrical characterization of the devices in dry state by using the bottom Si gate before and after the mercury exposure (see **Figure 3a**). The results clearly demonstrate that the device response is regardless of mercury exposure. Thus, this indicates that only the semiconductor top surface is altered by Hg^{2+} .

Another key issue is to understand the role of PS in the OSC thin film and, therefore, the same experiments were performed with films prepared only with diF-TES-ADT, free of PS. The diF-TES-ADT-based WGOFET after mercury exposure displays a similar positive shift of V_{th} , but much more pronounced (see Figure S6, Supporting Information). More importantly, the OFET performance is significantly affected after having been exposed to the Hg^{2+} solution ($c = 10 \mu\text{M}$) when measured in dry conditions by using the Si back-gate, as shown in Figure 3b. Here, a strong current increase is observed and the current modulation capability of the device is drastically decreased. A similar behavior was also observed by Bao *et al.* on a DDFTTF-based OFET (DDFTTF stands for 5,5'-bis-(7-dodecyl-9H-fluoren-2-yl)-2,2'-bithiophene) and was tentatively attributed by the authors to the doping effect of Hg^{2+} itself or to the formation of a charge transfer complex between Hg^{2+} and the semiconductor.^[26] Considering these results, it can be unambiguously affirmed that the PS encapsulation layer is crucial for avoiding the penetration of the ions into the bulk of the OSC film.

As mentioned, a possible explanation of the response of the WGOFET device to the presence of Hg^{2+} can be ascribed to the redox reaction occurring between Hg^{2+} and

semiconductor molecules at the first surface layers where charge accumulation takes place, as shown in **Figure 4a**. Kim and co-workers have already shown that single-walled carbon nanotube-based FETs respond in a similar manner to Hg^{2+} proving the preferential chemical interaction of this divalent metal to carbon nanotubes.^[27] Such behavior can be justified if we consider the standard oxidation potential of Hg^{2+} (0.8535 V *vs* NHE) that is significantly larger compared to the other reference metal ions (*e.g.* $\text{Ca}^{2+} = -2.924$ V, $\text{Mg}^{2+} = -2.372$ V, $\text{Mn}^{2+} = -1.185$ V, $\text{Zn}^{2+} = -0.7628$ V, $\text{Fe}^{2+} = -0.44$ V, $\text{Pb}^{2+} = -0.126$ V, $\text{Cu}^{2+} = 0.159$ V *vs* NHE).^[27,28] Taking this into account, we should expect to observe the same p-doping behavior with other p-type semiconductors. Thus, the experiments were repeated changing the OSC of the organic blend with TIPS-pentacene (*i.e.*, 6,13-Bis(triisopropylsilylethynyl)pentacene), a semiconductor having a similar highest occupied molecular orbital (HOMO) level to diF-TES-ADT. As depicted in Figure S7 (Supporting Information), the electrical response of TIPS-pentacene based WGOFET remains practically identical to the one found with diF-TES-ADT. To further confirm the redox mechanism, another metal cation (Fe^{3+}) possessing less oxidation capability (oxidation potential is 0.77 V *vs* NHE) has been used as target.^[28] *I-V* characteristics did not show any shift after being exposed to 1 mM of Fe^{3+} ions (Figure S8a, Supporting Information), and only the same behavior is visible when the Fe^{3+} concentration is increased up to 50 mM (Figure S8b, Supporting Information). Such evidence supports the fact that a less oxidizing agent induces a similar effect only at higher concentration. Hence, we can safely state that even though an aspecific interaction is occurring between the OSC and Hg^{2+} , by selecting an OSC with an appropriate HOMO level and establishing a definite experiment protocol (*i.e.*, exposure time or working ion concentration range), we can impart an effective selectivity to this electronic transducer. Keeping in mind that this metal ion represents one of the most aggressive pollutants in nature,^[29] we can envisage that these devices could also be potentially exploited as in-field sensors after a wider screening of further interfering agents that are naturally contained in real polluted samples.

A schematic vision of the redox process that is taking place on the OSC/water interface is illustrated in **Figure 4**. The electron transfer process increases the number of positive charge carriers (*i.e.*, holes) in the channel. This kind of carriers can be called as doping-induced holes. To further support the above mentioned mechanism, we have performed a series of experiments aiming to study the top of thin-film surface. Kelvin Probe Force Microscopy (KPFM) is a valuable technique to measure the work function or electrical surface potential of a semiconductor in nanometer-scale.^[30] By means of KPFM the contact potential difference (V_{CPD}) between the tip and the semiconductor prior to and after exposure to Hg^{2+} solution was measured. The V_{CPD} is defined as $V_{CPD} = \frac{\phi_{tip} - \phi_{sample}}{-e}$, where e is the electronic charge and ϕ_{tip} and ϕ_{sample} are the work-function of the tip and the semiconductor, respectively.^[30] For a semiconductor thin film, the measured V_{CPD} is related to the surface potential ($\phi_{surface}$), which differs from the work function of semiconductor materials due to the surface-charge limit near the semiconductor surface.^[30,31] As shown in **Figure 4a** and **b**, the V_{CPD} value can be extracted directly from the DC voltage applied to the sample when the electrical force is nullified, that is, $V_{CPD} = -V_{DC}$, where V_{DC} is the DC voltage applied to the sample (see Methods). Therefore, with the same tip acting as the reference, the measured V_{CPD} change ($\Delta V_{CPD} = V_{CPD}^{Hg^{2+}} - V_{CPD}^{initial}$) reflects the surface potential change of the sample after Hg^{2+} exposure. The extracted average DC voltages are summarized in Table S3 (Supporting Information), where - 69 mV and - 99 mV are the ΔV_{CPD} corresponding to the OSC blend thin film on the Au electrode and SiO_x regions, respectively. The decrease of the surface potential both in the OSC-coated Au electrode and SiO_x area after exposure to the Hg^{2+} solution is in agreement to the above-mentioned p-type surface doping (details are provided in the Supporting Information). For comparison, the ΔV_{CPD} values do not show any apparent change when the thin film is exposed to Zn^{2+} (see Figure S9a,b, Supporting Information).

To further understand the influence of the p-type surface doping on the OSC, electrochemical impedance spectroscopy has been employed to study the double layer capacitance at the water/OSC interface.^[19] For the WGOFET, the total electrical double layer capacitance C_{dl} is the result of two capacitances in series, *i.e.* gate/water capacitance (C_1) and water/OSC capacitance (C_2), $\frac{1}{C_{dl}} = \frac{1}{C_1} + \frac{1}{C_2}$. In general, the gate/water capacitance ($C_1 \sim$ tens of $\mu\text{F}/\text{cm}^2$) is larger than the water/OSC capacitance (C_2 is a few $\mu\text{F}/\text{cm}^2$).^[23] Therefore, when WGOFET channel is depleted C_2 dominates, whereas in accumulation the two capacitances can be assumed roughly comparable. The plot of C_{dl} vs f response recorded with the device in the off-state condition (DC voltage set to 0.3 V) shows a remarkable difference response between the untreated substrate and the Hg^{2+} treated one ($c = 1 \text{ mM}$) due to the presence of doping-induced charges, whereas the response in on-state condition (DC voltage set to -0.3 V), remains practically unchanged ($5.3 \mu\text{F}/\text{cm}^2$ at 10 Hz, as shown in Figure 4c, d). This behavior is attributed to the high charge carrier density present in the channel where WGOFET is in accumulation regime that dominates the effective interface capacitance and the contribution of the carriers induced by the doping process become less relevant. In addition, the constant capacitance response in the accumulation regime (see Figure 4d) further agrees with the fact that the product $\mu_{FET} \cdot C_{dl}$ is not altered in the reported WGOFETs after Hg^{2+} exposure and only a potentiometric shift in the curves is effectively observed (see Figure S2, Supporting Information). Again for comparison, the same experiments were carried out by treating the devices with a Zn^{2+} solution ($c = 1 \text{ mM}$) and no detectable changes were observed (Figure S9c,d, Supporting Information). In other terms, the total capacitance remains unaltered in both operating conditions.

3. Conclusion

In conclusion, we have fabricated water-gated field-effect transistor based on the organic semiconductor dif-TES-ADT blended with polystyrene. By exposing the OSC thin

film to an aqueous solution containing Hg^{2+} , p-type surface doping in the organic semiconductor thin film has been achieved due to a redox reaction between Hg^{2+} and the semiconductor surface. This doping mechanism is supported by KPFM and electrochemical measurements. As a result, V_{th} of the WGOFET shifts to positive gate voltage, which exhibits a linear detection response towards Hg^{2+} in a concentration range spanning from nanomolar to millimolar. Furthermore, the redox reaction of the organic semiconductor with Hg^{2+} seems to be limited to this cation in concentrations range up to 1 mM and no interfering effects have been observed in the presence of other divalent cations. It should be highlighted that the detection limit of 1 nM towards Hg^{2+} is comparable to other fluorescence sensors and biosensors reported in literature^[32–34] and satisfies the U. S. Environmental Protection Agency standards in terms of Hg^{2+} contamination in drinking water.^[26,32] Thus, the implementation of a blended p-type OSC with a proper HOMO level in a WGOFET offers an excellent platform to develop simple and portable electronic devices for Hg^{2+} detection.

4. Experimental Section

Materials: 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TES-ADT) and 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) was purchased from Lumtec. and Ossila, respectively. Polystyrene ($M_w \sim 10,000 \text{ g mol}^{-1}$), chlorobenzene (CB), 2,3,4,5,6-pentafluorothiophenol (PFBT) and all the metal chloride salts (also including $\text{Pb}(\text{NO}_3)_2$) were purchased from Sigma-Aldrich and used without any further purification. Polydimethylsiloxane (PDMS) was purchased from Dow Corning Corporation and prepared according to the standard protocol (Sylgard® 184 for more information see: www.dowcorning.com). Platinum (Pt) wire ($\phi = 0.5 \text{ mm}$) was purchased from Sigma-Aldrich and was cleaned in hot sulphuric acid (0.1 M) for 30 minutes and rinsed with MilliQ water (resistivity: $18.2 \text{ M}\Omega \cdot \text{cm}$) prior to each electrical and electrochemical measurement.

Device fabrication: A heavily doped n-type silicon wafer featuring thermal SiO_x (200 nm thick) was used as substrate. The source and drain (S/D) electrodes were patterned by photolithography (MicroWriter MLTM Laser Lithography System) and a metallic layer of Cr/Au (5 nm/40 nm) was subsequently evaporated (Evaporation System Auto 360 from BOC Edwards). The channel width (*W*) and length (*L*) were 20700 μm and 30 μm (the geometrical ratio *W/L* = 690), respectively. Prior to the deposition of organic thin film, the substrates were cleaned in ultrasonic bath with acetone and isopropanol for 15 min, respectively. Substrates were further cleaned with UV-ozone for 25 min and immersed in a 15 mM solution of PFBT in isopropanol for 15 minutes. The OSC and polymer were mixed in a 4:1 ratio, and then dissolved in chlorobenzene reaching a final concentration of 2 wt%. The blend solution was kept on a hot-plate at 105 °C for 1 h to completely dissolve the two components. The OSC:polymer solutions were deposited in ambient conditions by BAMS at a fixed speed of 1 cm s⁻¹ and keeping the base plate temperature at 105 °C.

Electrical measurements: All the electrolyte-gated and back-gate electrical measurements were performed with an Agilent 5100A SMU through Easy Expert software. The liquid electrolyte was confined on the interdigitated region by means of a PDMS pool (volume was equal to 20 μL) with a Pt wire serving as top gate electrode. All the transfer characteristics were recorded in linear and saturation regime (*V*_{DS} = -0.1V and -0.3 V) in a MilliQ water media. Before metal ions test, each WGOFET has been characterized in MilliQ water with a standard *I-V* transfer in order to assess its electrical stability. Back gate measurements were performed using n-doped Si/SiO_x as gate electrode and dielectric, respectively. In order to exclude any interaction of metal ions with SiO_x channel and S/D contacts, back-gate electrical tests were performed before and after each WGOFET experiment. All the WGOFET and back-gate measurements were performed in ambient conditions.

Metal-ion solutions preparation and Hg^{2+} -mediated surface doping protocol: All metal ion-containing solutions (1 mM) were prepared by dissolving the corresponding metal chloride salts in MilliQ water. Due to the poor water solubility of PbCl_2 , the corresponding nitrate salt ($\text{Pb}(\text{NO}_3)_2$) was chosen as interfering agent. In order to study the electrical response of OSC:polymer thin-film towards Hg^{2+} -ions, devices were exposed to five different HgCl_2 solutions (1 mM, 50 μM , 1 μM , 50 nM, and 1 nM) in ascending order. A drop of HgCl_2 solution (35 μL) was placed on top of the active transistor area and kept for 3 min. Then, the samples were carefully rinsed three times with MilliQ water and dried under nitrogen stream. The detection of other reference metal ion solutions were realized following the same procedure. All the metal-ion-containing solutions were freshly prepared before each experiment and the detection tests were completed in ambient conditions.

Electrochemical impedance spectroscopy (EIS) measurement and kelvin probe force microscopy (KPFM): For the EIS measurements, S/D electrodes were short-circuited and kept ground to serve as counter electrode while, Pt wire was immersed into MilliQ water in the PDMS pool to act as working electrode. EIS spectra were recorded with a Novocontrol Alpha-An impedance analyzer equipped with POT/GAL 30V/2A electrochemical interface in a frequency range of $10^5 \sim 10^{-1}$ Hz. The DC voltage spanned from 0.7 V to -0.3 V with a step of -0.1 V and was superimposed on an AC signal of 10 mV. KPFM measurements were obtained with a 5500LS SPM from Agilent Technologies in amplitude mode by applying an AC voltage (V_{AC}) plus a DC voltage (V_{DC}) to the sample. Each OSC:PS film sample contains two regions of interest: the first one is the ion-exposed region prepared according to the aforementioned protocol, while the second one was kept unaltered and it represents the reference zone in the KPFM measurements. The CPD tests were performed on OSC-coated Au electrode and OSC-coated SiO_x in the interdigital area, respectively. The V_{AC} generates

oscillating electrical forces between the AFM tip (Au) and sample surface, and V_{DC} nullifies the oscillating electrical forces that originated from CPD between tip and sample surface. The equation used to measure the V_{CPD} is: $F_{\omega} = -\frac{\partial C(z)}{\partial z}(V_{DC} \pm V_{CPD})V_{AC}\sin(\omega t)$, where the $\pm$ sign depends whether the bias (V_{DC}) is applied to the sample (+) or the tip (-).^[30] In our measurement, the bias is applied to the sample, which indicates the sign is +.

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Figure 1. Schematic procedure of the surface transfer doping process presented in this work. a) Chemical structures of the semiconductor molecule used as active material for WGO FET preparation. b) WGO FET architecture measured in MilliQ water representing the initial step of our experiment protocol. c) WGO FET platform exposed to Hg^{2+} solutions and d) WGO FET setup characterized after Hg^{2+} treatment. e) I - V characteristics treated with different $[\text{Hg}^{2+}]$. f) Threshold voltage shifts ΔV_{th} vs Hg^{2+} concentrations. The sample is exposed to Hg^{2+} from 1 nM to 1 mM in ascending order.

Figure 2. Response of the WGOFET platform towards Hg^{2+} and several interfering divalent cations. The I - V transfer characteristics prior to and after exposure to a) a solution of a single metal ion (Zn^{2+}), b) a solution with a mixture of $\text{Zn}^{2+} + \text{Hg}^{2+}$, c) a solution of six different metal ions and d) the same solution where Hg^{2+} is also present. The concentration of the ions solutions is 1 mM. All the black curves represent the response of the device prior the exposure to metal ions, the red curves represent the response of the device toward a Hg^{2+} -containing solution and blue ones refers to experiments where no Hg^{2+} has been used.

Figure 3. I - V transfer characteristics (dry state) before and after exposure to MilliQ water and Hg^{2+} solution using bottom gate configuration. The OFET characteristics record with a) diF-TES-ADT:PS blend-based device and b) only diF-TES-ADT-based one.

Figure 4. Schematic diagram of redox reaction and p-type surface doping. a) Schematic representation of the redox reaction between semiconductor and Hg^{2+} ions solution. b) Surface induced charges on the top of semiconductor thin film generated by the redox reaction.

Figure 5. CPD and capacitance measurements recorded before (black square) and after (red circle) Hg^{2+} treatment of the OSC blend thin-film. CPD scans on a) OSC-coated Au electrode and on b) OSC-coated SiO_x area in the interdigitated region. Capacitance measurements of the same WGO-FET platform recorded at c) $V_{\text{DC}} = 0.3$ V (channel OFF) and d) on-state, $V_{\text{DC}} = -0.3$ V (channel ON).

Supporting Information

Mercury-mediated organic semiconductor surface doping monitored by electrolyte gated field effect transistors

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Figure S1 Transfer characteristic cycles showing the stability of the WGOFET platform (a) before and (b) after exposure to Hg^{2+} ion solution (1 mM). (c) Output characteristics before and after exposure to Hg^{2+} solution (1 mM).

Figure S2 (a) Lin-Lin plot of transfer curves of Fig. 1c. (b) Shifting of transfer curves along the V_{GS} axis showing the perfect overlap of the curves with their reference device (*i.e.*, without Hg^{2+} exposure). (c) $I^{1/2}$ vs V_{GS} transfer characteristic showing transfer curves after exposure to different concentration of Hg^{2+} . (d) Box-chart plot showing the ΔV_{th} trend.

Figure S3 (a) I - V transfer characteristics recorded in linear regime ($V_{DS} = -0.1$ V) prior to and after exposure to aqueous solutions of different Hg^{2+} concentrations. (b) Estimation of the surface charge carriers induced by mercury doping (values extracted in linear regime $V_{DS} = -0.1$ V).

Figure S4 I - V transfer characteristics prior to and after exposure to different solutions containing six different divalent cations (1 mM). All the black (red) curves represent the transfer characteristics before (after) exposure to the cations solutions.

Figure S5 I - V transfer characteristics prior to and after exposure to solutions containing a mixture of different metal ions (total concentration equal to 1 mM).

Figure S6 I - V transfer characteristics of diF-TES-ADT devices free of PS recorded in electrolyte gating. The experiments points out the role of PS present in the active layer and how it prevents ion penetration in the bulk of the OSC thin film.

Figure S7 I - V transfer characteristics of TIPS-pentacene:PS blends treated with Hg^{2+} solutions.

Figure S8 I - V transfer characteristics prior to and after exposure to Fe^{3+} solutions; (a) $[\text{Fe}^{3+}]$ 1 mM and (b) $[\text{Fe}^{3+}]$ 50 mM .

Figure S9 KPFM and capacitance results prior to (black square curves) and after (blue circle curves) exposure to 1 mM Zn^{2+} solutions. CPD curves are recorded on (a) OSC-coated Au electrode and (b) OSC-coated SiO_x area (interdigitated region). Capacitance measurements of the same WGO/FET platform recorded in (c) off-state (DC = 0.3 V) and (d) on-state (DC = -0.3 V).

The qualitative explanation of the relationship between the KPFM results and p-type doping:

The p-type doping effect due to the redox reaction between Hg^{2+} and the semiconductor molecules results in a localized Fermi level shift towards the HOMO band. As a consequence,

in order to nullify the surface charge, a higher DC voltage is required and a positive shift in the amplitude curve is observed.

Table S1. Field effect mobility extracted from Fig. 1c after exposure to different HgCl_2 solutions. C_{dl} value used here was extracted from Fig. 5d at 10 Hz.

Hg^{2+} concentration	Slope ($\times 10^{-3}$)	intercept ($\times 10^{-3}$)	V_{th} (mV)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	μ_{FET} ($\times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	$\mu_{FET} * C_{dl}$ ($\times 10^{-2} \mu\text{F V}^{-1} \text{ s}^{-1}$)
MilliQ	-8.9	3.5	392	5.3	4.3	2.3
1 nM	-8.8	3.6	407	5.3	4.3	2.3
50 nM	-9.1	4.0	440	5.3	4.5	2.3
1 μM	-9.1	4.3	473	5.3	4.4	2.3
50 μM	-8.7	4.5	517	5.3	4.2	2.2
1 mM	-8.6	5.1	585	5.3	4.2	2.2

Table S2. ΔV_{th} shifts after exposure to Hg^{2+} extracted from 10 devices.

ΔV_{th}	1 nM (mV)	50 nM (mV)	1 μM (mV)	50 μM (mV)	1 mM (mV)
1 [#]	23	55	87	164	201
2 [#]	12	56	56	122	174
3 [#]	6	26	73	120	210
4 [#]	42	88	112	199	237
5 [#]	5	55	100	164	180
6 [#]	24	68	87	129	132
7 [#]	37	76	119	181	256
8 [#]	3	38	43	83	101
9 [#]	9	33	84	108	115
10 [#]	15	48	82	124	193

Table S3. Average V_{CPD} values extract prior to and after exposure to Hg^{2+} and Zn^{2+} solutions at the same concentration.

Type of ion	Area	intercept	slope	V_{Bias} (V)	$V_{Bias,average}$ (V)	$V_{CPD,average}$ (V)
$HgCl_2$ (1 mM)	Au area (bare)	-0.041	0.091	0.451	0.443	-0.443
		-0.041	0.091	0.439		
		-0.041	0.091	0.441		
	Au area (Hg^{2+} -exposure)	-0.047	0.093	0.506	0.512	-0.512
		-0.048	0.093	0.515		
		-0.048	0.093	0.514		
	SiO_x area (bare)	-0.035	0.082	0.432	0.433	-0.433
		-0.035	0.081	0.432		
		-0.035	0.081	0.432		
	SiO_x area (Hg^{2+} -exposure)	-0.034	0.065	0.519	0.532	-0.532
		-0.035	0.065	0.538		
		-0.035	0.065	0.538		
$ZnCl_2$ (1 mM)	Gold area (bare)	0.158	-0.323	0.489	0.494	-0.494
		0.156	-0.321	0.488		
		0.163	-0.323	0.504		
	Gold area (Zn^{2+} -exposure)	0.167	-0.332	0.504	0.497	-0.497
		0.163	-0.329	0.496		
		0.172	-0.351	0.491		
	SiO_x area (bare)	0.081	-0.301	0.274	0.281	-0.281
		0.084	-0.299	0.283		
		0.084	-0.295	0.287		
	SiO_x area (Zn^{2+} -exposure)	0.091	-0.299	0.302	0.287	-0.287
		0.073	-0.276	0.265		
		0.087	-0.299	0.293		