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## A mercury (II) ion sensor device based on an organic field effect transistor with an extended-gate modified by dipicolylamine

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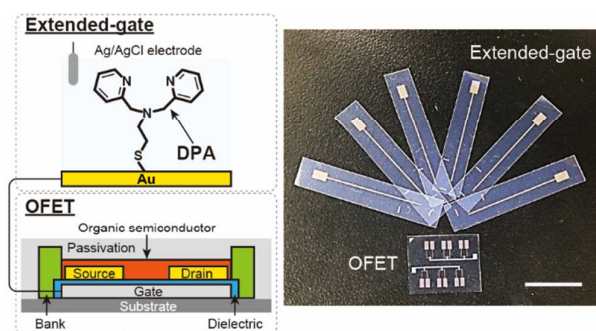
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Herein, we report an organic field effect transistor (OFET) with an extended-gate modified by an artificial receptor for the detection of mercury (II) ion ( $\text{Hg}^{2+}$ ) in water. The sensor device is easy-to-fabricate, reusable, disposable, and portable. Thus OFET sensors could be applied for low-cost on-site detection of  $\text{Hg}^{2+}$ .

Heavy metal pollution is one of the significant environmental problems. Mercury, which is found as metallic, inorganic, and organic forms, is recognised as a highly toxic pollutant.<sup>1</sup> Mercury (II) ion ( $\text{Hg}^{2+}$ ) may be converted into organic mercuric compounds, causing damage in organs such as brain, kidney, liver and nervous systems. Hence, the detection of  $\text{Hg}^{2+}$  is very important for preservation of healthy lives. Although several highly sensitive and accurate methods such as atomic absorption spectroscopy (AAS),<sup>2</sup> atomic fluorescence spectrometry (AFS),<sup>3</sup> and inductively coupled plasma mass spectrometry (ICP-MS)<sup>4</sup> have been developed, these methods are high-cost, and their application is time-consuming and requires sophisticated instrumentation. Thus, simpler and easier methods are desirable.

Toward this end, colourimetric,<sup>5</sup> fluorometric<sup>5</sup> or electrochemical<sup>6</sup>  $\text{Hg}^{2+}$  detection based on supramolecular interactions is vigorously researched. In many cases, their sensitivity and selectivity for  $\text{Hg}^{2+}$  has been mainly investigated. However, the manufacturing costs of the  $\text{Hg}^{2+}$  sensors have not been discussed. Although some unique and intriguing  $\text{Hg}^{2+}$  sensors could be found, their potential industrial mass production seems difficult. In this regard, we strongly believe that organic field effect transistors (OFETs)<sup>7</sup> are one of the prospective candidates for the sensing of  $\text{Hg}^{2+}$ . Based on solution-processes, the OFETs can be fabricated on various types of substrates including plastic films, glass, and paper,

etc. The photolithography, crystallisation at high temperature, or



**Fig. 1** Schematic structure of the  $\text{Hg}^{2+}$  sensor based on the extended-gate type OFET. The extended-gate electrode is modified with dipicolylamine self-assembled monolayer. A photograph shows the fabricated sensing devices (six devices in the picture). The scale bar corresponds to 2 cm.

silicon substrates are not required, which means that the fabrication of OFET-sensors is easy, environmentally-friendly and low-costs. Although a heavy metal ion sensor based on an OFET modified with a DNA-probe has been recently reported,<sup>8</sup> OFET sensors modified with artificial receptors for  $\text{Hg}^{2+}$  are underdeveloped. Here, we report the first extended-gate type OFET sensor for the  $\text{Hg}^{2+}$  detection in aqueous media. The fabricated OFET possesses a thiolated-dipicolylamine<sup>9</sup> (DPA) derivative which can coordinate mercury (II) ion.<sup>10</sup>

The device structure of the OFET-sensor is shown in Fig. 1. The extended-gate electrode was made of thin layer of gold on a plastic film. The gold surface was modified with a thiolated DPA self-assembled monolayer (SAM). Solution-processable poly{2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-b]thiophene} (pBTTT-C<sub>16</sub>)<sup>11</sup> was employed as the OFET active layer, which delivers stable and reproducible operation. The details of the OFET fabrication are summarised in Electronic Supplementary Information (ESI). The modification of the extended-gate electrode was performed by immersing the electrode in a methanol solution of the thiolated DPA. The extended-gate electrode was characterised by photoelectron spectroscopy, wettability and variable angle spectroscopic ellipsometry measurements (see the ESI for details).

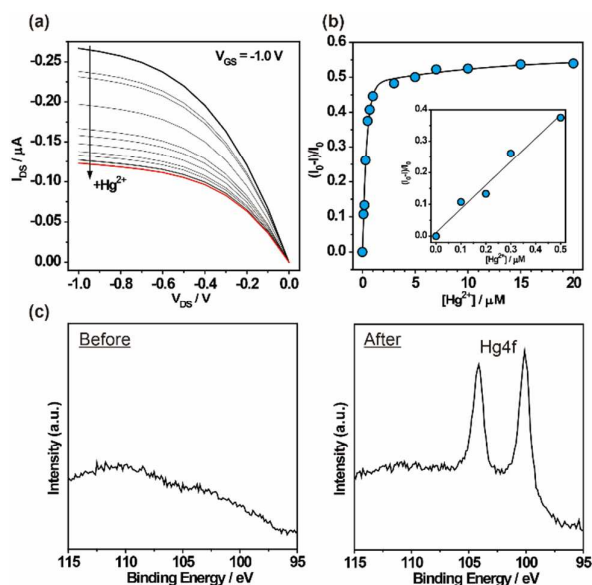
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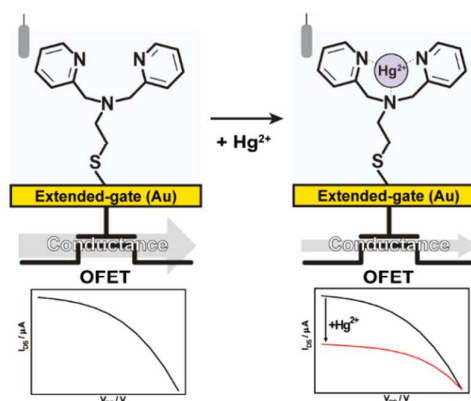
†Electronic Supplementary Information (ESI) available: General information of experiments, fabrication of the OFET device, modification of the extended-gate electrode, electric characteristics of the OFET, the relationship of drain currents and metal ion titrations. See DOI: 10.1039/x0xx00000x. See DOI: 10.1039/x0xx00000x

The electric properties of the DPA-modified extended gate OFET were investigated, revealing that the device could operate at below 1 V. In addition, repetitive measurements showed that the OFET was stable against the bias stress. (See the ESI). Based on these results, we concluded that the OFET can be employed as a heavy metal ion sensor.

Next, we attempted to detect  $\text{Hg}^{2+}$  in water. The extended-gate electrode was immersed in an aqueous solution of  $\text{Hg}(\text{NO}_3)_2$ . The gate voltage was applied through a silver/silver chloride electrode (Fig. 1). Figs. 2a exhibits the output characteristics of the OFET upon addition of incremental amounts of  $\text{Hg}^{2+}$  in a HEPES (= 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution with NaCl (100 mM), pH 7.4 at r.t. As a result, the output current decreased with increased the concentration of  $\text{Hg}^{2+}$ . Fig. 2b summarises the relationship between the  $\text{Hg}^{2+}$  concentration and change in the output current. The function mechanism of extended-gate type FETs is based on a shift in the surface potential at the extended-gate electrode/solution interface.<sup>12</sup> The channel conductance of the extended-gate type FETs is mainly determined by the potential difference between the reference and the extended-gate electrodes. Thus, these observed changes of the output current stem from changes in conductance within the OFET channel affected by the positively charged mercury ions ( $\text{Hg}^{2+}$ ) captured on the extended-gate electrode (Fig 3). As an evidence of the capture of  $\text{Hg}^{2+}$  by DPA, we measured X-ray photoelectron spectroscopy (XPS) of the extended-gate electrode after the immersion in the  $\text{Hg}^{2+}$  solution. As expected, XPS indicated the presence of mercury with its expected binding energy (Fig. 2c), which strongly supported that the electrical changes in the OFET characteristics were caused by the captured  $\text{Hg}^{2+}$ . Furthermore, it is



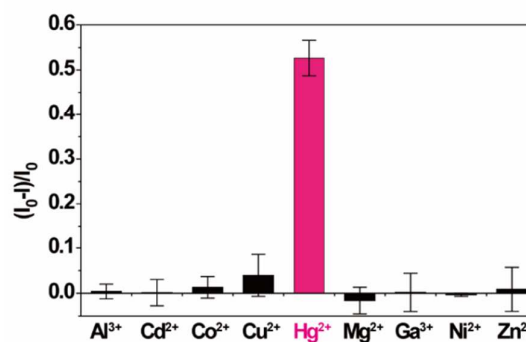
**Fig. 2.** (a) Output characteristics ( $I_{DS}$ - $V_{DS}$ ) of the OFET upon addition of incremental amounts of  $\text{Hg}^{2+}$  in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4 at r.t. [ $\text{Hg}^{2+}$ ] = 0–20  $\mu\text{M}$ . (b) Titration isotherm corresponding to the  $\text{Hg}^{2+}$ -induced  $I_{DS}$  change. (c) XPS spectra of the Hg4f region of the DPA-modified gold electrode before and after the immersion in the aqueous solution with  $\text{Hg}^{2+}$ . As pretreatment of the XPS measurement, the immersed gold electrode was carefully washed up by water (without  $\text{Hg}(\text{NO}_3)_2$ ).



**Fig. 3.** A plausible detection mechanism of  $\text{Hg}^{2+}$  by the fabricated OFET. The DPA on the extended-gate electrode captures  $\text{Hg}^{2+}$ , which induces the decrease of the conductance within the OFET.

worth noting that the detection of  $\text{Hg}^{2+}$  was successfully achieved even in the presence of large excess of interferent  $\text{Na}^+$  (100 mM). The detection limit<sup>13</sup> of  $\text{Hg}^{2+}$  was estimated to be 9.9 ppb, which is comparable to or lower than those of recent reported sensors based on colourimetric,<sup>14</sup> fluorometric,<sup>15</sup> and electrochemical<sup>16</sup> systems. Although the detection limit is slightly higher than WHO's guideline value for inorganic mercury in drinking water,<sup>17</sup> the further improvement of sensitivity could be attained by OFET-based electronic circuits such as amplifiers.<sup>18</sup>

The next step was to investigate the selectivity of the OFET sensor toward various metal ions. The extended-gate electrode of the OFET was immersed in the aqueous solutions of metal ions (such as  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ga}^{3+}$ , and  $\text{Al}^{3+}$ ) (3  $\mu\text{M}$ ) and the output current was measured. The OFET modified with DPA receptor senses the metal ions in the following order:  $\text{Hg}^{2+} \gg \text{Cu}^{2+} > \text{Zn}^{2+}$ ,  $\text{Ni}^{2+} \geq \text{Cd}^{2+} \gg$  other metal ions ( $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ga}^{3+}$ , and  $\text{Al}^{3+}$ ). The strongest response of the OFET to metal ions was to  $\text{Hg}^{2+}$  while  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  showed weak response (See the ESI). These responses are arising from the binding affinity of DPA for heavy metal ions. To improve the selectivity, we decided to add pyridine-2,6-dicarboxylic acid (PDCA)<sup>19</sup> in the sensing system. PDCA is a chelating agent that forms complexes with heavy metal ions

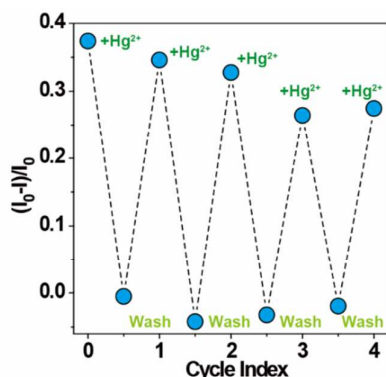


**Fig. 4.** Output current changes in the fabricated OFET sensor after adding of various metal ions in a HEPES buffer solution (10 mM) with NaCl (100 mM) and PDCA (1 mM), pH 7.4 at r.t. [Metal ion] = 3  $\mu\text{M}$ . Three repetitions were measured for each analyte using the same device.

such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$ . On the other hand, PDCA does not have an appreciable affinity to  $\text{Hg}^{2+}$  in aqueous solutions,<sup>20</sup> suggesting that the chelating ability of PDCA would be very suitable to improve the selectivity of the OFET sensor. As expected, the response to  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  was dramatically decreased in the presence of PDCA, while we still observed significant changes in the output current upon addition of  $\text{Hg}^{2+}$  (Fig. 4). It is noteworthy that our sensing system based on the OFET with DPA does not require any biomolecules (e.g. DNA probes, enzymes, or antibodies), which implies higher chemical stability in a long-term use and storage.

To confirm further practical utility of the sensing system, a competitive experiment was carried out. We attempted to detect  $\text{Hg}^{2+}$  in an aqueous solution in the presence of 9 competing metal ions ( $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ga}^{3+}$ , and  $\text{Al}^{3+}$ ). The OFET with PDCA showed a clear response to  $\text{Hg}^{2+}$  even in the presence of competitive metal ions. (See the ESI). This confirmed that the effect of potentially interfering ions in the  $\text{Hg}^{2+}$  sensing is almost negligible.

Finally, we have investigated the reusability of the OFET sensor device. The electrical response could be recovered by rinsing of the extended-gate electrode with an aqueous solution of ethylenediaminetetraacetic acid (EDTA). The reusability was investigated by alternatively immersing the electrode in an aqueous solution containing  $\text{Hg}^{2+}$  and EDTA, which resulted in an efficient electrical switching. As illustrated in Fig. 5, the drain current could be recovered when the electrode was immersed in EDTA solution for 20 min at r.t. This is a result of a competitive binding between the DPA and EDTA toward  $\text{Hg}^{2+}$ . This suggests that the device is reusable and also that no dramatic degradation of the OFET takes place in repeated use.



**Fig. 5.** Changes in the output current upon alternating treatment by aqueous solutions of  $\text{Hg}^{2+}$  and EDTA. The standard deviation of each response is < 2%.

In summary, we have successfully developed a reusable  $\text{Hg}^{2+}$  sensing system based on an extended-gate type OFET. The sensitivity of the fabricated OFET is comparable to or higher than those of optical or electrochemical sensing systems. Importantly, the extended-gate electrode was fabricated on a plastic film, suggesting that the fabricated electrode could be used in a disposable fashion. Thus, our preliminary results indicate that the extended gate OFETs could open up a new avenue in the development of low-cost, reusable and disposable  $\text{Hg}^{2+}$  sensor devices. Furthermore, modifications of the periphery of the OFET

could yield more efficient systems. Experiments to this effect are in progress in our laboratory.

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